

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

221.1/000-213

FINAL TECHNICAL REPORT

CHARGED PARTICLE RADIATION DAMAGE IN SEMICONDUCTORS, XIII:

EFFECT OF LITHIUM IN IRRADIATED SILICON

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

25 MAY 1968

10971.6002-R000

Hard copy (HC) 3.00

Microfiche (MF) .65

653 July 65

Contract No. NAS5-10322

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GODDARD SPACE FLIGHT CENTER

FACILITY FORM 602

N 68-28996
(ACCESSION NUMBER) (THRU)
74 (PAGES) 1 (CODE)
✓ (NASA CR OR TMX OR AD NUMBER) 26 (CATEGORY)



TRW
SYSTEMS GROUP

ACKNOWLEDGEMENTS

This report covers work performed under Contract NAS5-10322 during the period from 27 January 1967 to 27 May 1968. We would like to acknowledge the helpful guidance of, and discussions with, Mr. Milton Schach, Dr. Pao Fang, and their associates of NASA-Goddard Space Flight Center during the conduct of this program. We would also like to acknowledge the cooperation and assistance of the many semiconductor organizations who provided the material and devices upon which these studies were based.

ABSTRACT

An experimental program has been conducted to evaluate the effects of electron irradiation on lithium solar cells. Considerable progress has been made in optimizing the technique of diffusing lithium into the devices and selecting starting materials. The best lithium cells compare favorably with n/p solar cells in an electron environment. The lithium cells are significantly superior to n/p solar cells under fast neutron bombardment. Capacitance measurements were used to study lithium distributions and concentration changes under different thermal conditions. The recovery kinetics were re-examined and the experimental evidence supports first order behavior for the case of the lithium concentration much greater than the defect concentration. Other miscellaneous studies were done to evaluate the effect of different dopants on radiation resistance of silicon.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. CELL EVALUATION STUDIES	2
III. LITHIUM DISTRIBUTION STUDIES	11
IV. RECOVERY KINETICS STUDIES.	15
V. OTHER IMPURITY STUDIES.	19
VI. SUMMARY.	21
TABLE I. LITHIUM CELL DATA	22
FIGURES 1 - 44	23 - 66

REFERENCES

1. V. S. Vavilov, Radiation Damage in Semiconductors, p. 115, Academic Press, New York 1964
2. J. J. Wysocki, IEEE Transactions on Nuclear Science NS-13, 6, 168 (1966).
3. J. R. Carter, Jr. and R. G. Downing "Radiation Damage in Lithium Doped Silicon and Silicon Solar Cells," Contract 08377-6005-R000 (28 Aug. 1966)
4. G. D. Watkins and J. W. Corbett, Physical Review 121, 1001 (1964).
5. W. Rosenzweig, Bell Systems Tech. J. 41, 1573 (1962).
6. W. MacDonald, et al., Semiconductor Products, Nov. 1959.
7. T. R. Waite, Physical Review 107, 463 (1957).
8. E. L. Ralph, et al., Investigation of Lithium Doped Hardened Solar Cells, August 1967.
9. J. O. McCaldin, Progress in Solid State Chemistry, Vol. 2, p. 9, Pergamon Press, New York (1965).

LIST OF ILLUSTRATIONS

<u>FIGURE</u>	<u>TITLE</u>
1	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
2	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
3	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
4	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
5	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
6	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
7	Effect of Storage Temperature on Recovery, 25°C
8	Effect of Storage Temperature on Recovery, 45°C
9	Effect of Irradiation Immediately after Manufacture
10	Effect of Irradiation Three Months after Manufacture
11	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells, 500°C Diffusion
12	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells, 500°C Diffusion
13	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells, 400-425°C Diffusion
14	Recovery of Short Circuit Current of Irradiated Centralab Lithium Solar Cells
15	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
16	Recovery of Short Circuit Current of Irradiated Heliotek Lithium Solar Cells
17	Relationship of Lithium Cell Short Circuit Current to Donor Concentration at the Junction, Heliotek Cells
18	Relationship of Lithium Cell Short Circuit Current to Donor Concentration at the Junction, Centralab Cell

LIST OF ILLUSTRATIONS (CONT.)

<u>FIGURE</u>	<u>TITLE</u>
19	Redegradation of Lithium Solar Cells
20	Recovery of Quartz Crucible Lithium Solar Cells
21	Degradation and Recovery of Quartz Crucible Lithium Solar Cells
22	Degradation and Recovery of Lithium Solar Cells from First Neutron Irradiation
23	Comparative Recovery of Lithium Solar Cells from Neutron and Electron Irradiation
24	Relationship of Short Circuit Current and Diffusion Length for Unirradiated Lithium Solar Cells.
25	Relationship of Short Circuit Current and Diffusion Length for Electron Irradiated Lithium Solar Cells
26	Short Circuit Current - Diffusion Length Changes for Irradiation and Recovery of Q.C. Lithium Solar Cells
27	Relationship of Junction Capacitance and Donor Concentration
28	Capacitance - Voltage Relations of Lithium Solar Cell, Various Electron Irradiations
29	Donor Concentration Changes After Manufacture of Lithium Solar Cells
30	Donor Concentration Changes After Manufacture of Lithium Solar Cells
31	Donor Concentration Changes During Redistribution of Lithium Solar Cells
32	Capacitance - Voltage Relations During Redistribution of Lithium Solar Cells
33	Short Circuit Current Changes During Redistribution of Lithium Solar Cells
34	Recovery from Irradiation of Lithium Solar Cells with Low Temperature Redistribution
35	Comparison of Various Solid State Reaction Kinetics Equations
36	Recovery of Irradiated Lithium Doped F.Z. Si-Au Barrier Diodes

LIST OF ILLUSTRATIONS (CONT.)

<u>FIGURE</u>	<u>TITLE</u>
37	Recovery of Irradiated Lithium Doped O.C. Si-Au Barrier Diodes
38	Recovery Kinetics of Irradiated Lithium Solar Cell
39	Recovery Kinetics of Irradiated Lithium Solar Cell
40	Recovery Kinetics of Irradiated Lithium Solar Cell
41	Recovery Kinetics of Irradiated Lithium Solar Cell
42	Recovery Kinetics of Irradiated Lithium Solar Cell
43	Irradiation of a n/p Silicon-Germanium Alloy Solar Cell
44	Irradiation of Sodium Doped Silicon and Bismuth Doped Silicon

TABLES

I	Lithium Cell Data
---	-------------------

I. INTRODUCTION

This report culminates effort under Contract No. NAS5-10322 in the study of effect of lithium doping on the radiation resistance of silicon solar cells. Interest in this field began with Vavilov's report of a radiation resistant diode made with lithium doped, crucible grown silicon.¹ Wysocki reported lithium doped solar cells which degraded under electron irradiation, but rapidly recovered at room temperature.² Float zone silicon, with a characteristic lower oxygen concentration, was used to achieve this result. Our efforts have been directed toward the understanding of the mechanism of the recovery of damage and the definition of problem areas for further study. As a result of our work, the observation of recovery at room temperature has been extended to electron damaged cells made from crucible grown silicon. The effect of a recovery of damage followed by a degradation was identified. We have also demonstrated the feasibility of doping float zone and crucible silicon crystals with lithium in the melt. This lithium doped silicon was used to fabricate gold barrier diodes which also exhibited recovery of radiation damage at room temperature. This observation represents the only independent confirmation of the recovery effect of lithium in irradiated silicon by means other than those used by Wysocki. Considerable work was directed toward the study of damage in bulk lithium doped silicon. Through this work, it has been possible to identify several aspects of the bulk damage, including removal rates, time dependent removal, exponential removal and a proposed removal mechanism.³

The present concept of radiation damage involves stable configurations of displacement products (vacancies and interstitials) and impurity atoms. The Si-A or Si-B₁ center is an example of one such defect which has been studied extensively⁴. This defect is a complex of one vacancy and an oxygen atom and is suspected of playing an important role in recombination in electron irradiated n-type silicon. It is desirable to gain some knowledge as to whether the stable defects generated during irradiation differ when lithium is present, and what is the nature of the processes which annihilate the recombination centers during room temperature annealing. This paper reports the initial effort in a program intended to clarify the role of lithium in irradiated silicon.

II. CELL EVALUATION STUDIES

The early work on lithium solar cells identified several problem areas. The primary problem was the low electric output of the lithium cells. A second problem existed because the maximum recovered output of an irradiated lithium solar cell often was below that of a contemporary n/p cell given the same electron fluence. The tendency of irradiated lithium cells to regrade after recovering to a maximum output was also observed as a potential problem. In addition, it is possible to exhaust the recovery ability of the lithium cell by excessive irradiation. Our object, in this program, has been to study variations in the above behaviors, and possibly identify the manufacturing variables which will minimize the undesirable effects.

Since recovery and redegradation are time dependent effects, a proper study often involves very long periods of time. In some cases, we have observed significant changes in the degradation pattern 4000 hours after irradiation. Because of the known time dependent effects, there is reason to believe that laboratory irradiations may have somewhat different effects on lithium cells compared with those of irradiation with considerably lower rates. It is reasonable, however, to expect that laboratory studies will permit selection of the most promising lithium cell manufacturing techniques for a space flight evaluation.

An evaluation series of lithium float zone cells was processed by Heliotek with various diffusion cycles. All of the diffusion variations involved extended from a 5-minute diffusion to a 90-minute diffusion followed by a 120-minute redistribution. Previous reports have discussed the effects of these various diffusions on the output of lithium cells. The effect is again illustrated in Figure 1. The cells shown in this graph were all lithium diffused for 5 minutes at 425°C, followed by various redistributions. It can be seen that the initial short circuit currents of these cells are all approximately 30 ma/cm². These values are very high relative to the earlier lithium cells and compare well with current commercial n/p cells. Further examination of this plot clearly indicates the effect of the redistribution on the irradiation recovery of lithium cells. This plot displays the short circuit current of the electron irradiated lithium cells as a function of time elapsed after termination of the irradiation. The irradiations were performed with a 1 Mev Van de Graaff accelerator with a rate of approximately 10¹⁵ e/cm²-hr. The cells shown in Figure 1 were irradiated with 3 x 10¹⁴ e/cm² and stored at 25°C while periodic measurements were made. The short circuit current of all cells shown was degraded to approximately 15 ma/cm². The data shown in the insert on the figures includes the lithium diffusion temperature followed by the diffusion time and the redistribution time for each cell on the graph. The results for cells 1305 and 1306 show that the 5-minute diffusion with no redistribution produces a cell which does not recover from its irradiated condition during the observation period. The samples which received a redistribution treatment after the 5-minute diffusion exhibited a very pronounced recovery after electron irradiation. After about 100 hours, cells 1265 and 1266 recovered to a short circuit current of 27 ma/cm². Cells 1261 and 1262 recovered to a slightly lower output in a similar period. It is also noted that cells 1265 and 1266 did not regrade after recovery

during nearly 3000 hrs. of observation. The redistribution apparently allows sufficient lithium to diffuse into the active area of the cell to permit recovery, without lowering the initial output.

Figure 2 is a similar presentation for cells with 90-minute diffusions at 425°C. In this case the cells with no redistribution treatment have a considerably lower initial output, but show a pronounced recovery effect. It is obvious from the data that increased redistribution times produce cells with higher initial outputs and improved recovery behavior. Cells 1257 and 1258 have an initial short circuit current of about 28 ma/cm² and after recovery from an irradiation of 3×10^{14} e/cm² have a short circuit current of 26 ma/cm². The recovery was then followed by a redegradation to 24 ma/cm². This performance is somewhat poorer than the best cells as shown in Figure 1. It is of interest to note that in this case the redegradation appears to stabilize at a short current circuit value not too far below the maximum recovered value. Although the cells with 5-minute diffusion and 120-minute redistribution (1265, 1266) appear to be clearly superior to others of this group, it has more recently been noted that after an additional irradiation of 3×10^{15} e/cm² these same cells were degraded to a short circuit current of 11 ma/cm² and did not recover during several hundred hours of observation. Further study is necessary to clarify this behavior.

Previously mentioned diffusion studies of lithium solar cells were confined to temperatures of 425°C. To investigate the effects of lower temperature diffusions, a set of cells was fabricated with 350°C lithium diffusions. A similar radiation analysis was completed on the lower temperature cells. The irradiation recovery results are summarized in Figures 3 through 6. The various diffusion and redistribution times were the same as were used at 425°C. The data for cells diffused for 5 minutes is shown in Figure 3. The cells with no redistribution after a 5-minute diffusion show no recovery at room temperature after an irradiation of 3×10^{14} e/cm² during an observation period extending 500 hours. When a lithium redistribution of 60 minutes is included, these cells begin to recover after several hundred hours of storage. A redistribution of 120 minutes produced a cell which is half recovered after 500 hours. Comparison of this data with that in Figure 1 indicates that the effect of the lower lithium diffusion temperature is largely to slow the recovery process.

Figure 4 includes all the cells diffused for 30 minutes at 350°C with various redistributions. Figure 4 differs in appearance for 3 in that the curves of cells with redistribution are displaced to the left. This indicates decreased recovery time for cells with the longer diffusion. It can also be noted that the data Figure 4 has a distinct similarity to that in Figure 1. This can be explained by difference in the diffusion coefficient of lithium at 425°C and 350°C. The ratio of these diffusion coefficients are roughly 5 to 1. Since the diffusion times at the two temperatures are in the ratio of 1 to 6, the lithium profile is roughly equivalent in both groups of cells. In the case of cells No. 1633 and 1634, the 30-minute diffusion was insufficient to achieve a cell with that would recover from irradiation within the observation period. When a redistribution follows the lithium diffusion, the recovery characteristics are greatly improved. A redistribution of 60 minutes produces a cell which is half recovered in 50 hours at room temperature. The longer redistribution of

120 minutes decreases the half recovery time 10 hours. In both cases, the maximum recovered J_{sc} is roughly 24-25 ma/cm^2 .

The data for the irradiation and recovery of the cells diffused 90 minutes at 350°C are shown in Figures 5 and 6. With a 90-minute diffusion, no redistribution is necessary to achieve a recovery effect from an irradiation of $3 \times 10^{14} \text{ e/cm}^2$. In this case the added effect of the redistribution accelerates the recovery but not to the extent shown by cells with shorter diffusions. The 60-minute redistribution decreases the half recovery time to about 3 hours. The longer redistribution of 120 minutes decreases the half recovery time to roughly 5 hours. Apparently, an excessively long redistribution can lower the lithium concentration in the active area of the cell and thus slow the recovery kinetics. The maximum recovered J_{sc} is 22 to 23 ma/cm^2 for the cells diffused 90 minutes at 350°C for a $3 \times 10^{14} \text{ e/cm}^2$ irradiation. After recovery from the $3 \times 10^{14} \text{ e/cm}^2$ irradiation the cells shown in Figure 5 were re-irradiated with a fluence of $3 \times 10^{15} \text{ e/cm}^2$. The results of this irradiation and recovery are shown in Figure 6. Although the recovery was not complete when the graph was drawn, it appears that most of the cells will recover to a J_{sc} of 20 ma/cm^2 . In this case the redistribution treatment does not affect the recovery from the heavier electron fluence. The half recovery time from this irradiation is about 50 hours. This is considerably longer than that required for recovery from the lower fluence. The recovery time is still very short compared to the time required to accumulate an equivalent electron fluence in a space environment.

The data covering the cells fabricated with various lithium diffusion schedules is tabulated in Table I. The donor concentrations were determined by capacitance measurements. The lithium concentrations were determined by subtracting an assumed 2.5×10^{14} phosphorous atoms/ cm^3 (20 ohm-cm) from the measured donor concentration at the junction. The CV^n column indicates the voltage-capacitance relationship of the cells. For cells with CV^3 relation (linear graded junctions) the calculated lithium gradient is listed. The half recovery times from various irradiations are listed in the last columns. Several conclusions can be drawn from the data in Table I. It is apparent that capacitance measurements of these cells can be used to predict the recovery behavior of a lithium solar cell from irradiation. If the cell exhibits a CV^2 relationship and no lithium is detected at the junction, the cell will not recover from irradiation at a rate of practical interest or the recovery effect will be exhausted at a relatively low electron fluence. Cells with a CV^3 relationship will recover the effects of irradiation much faster and will recover from larger fluences of electrons.

A few points should be noted in these studies. It is very significant that, despite all the variations inherent in the cells produced for these lithium diffusion studies, an irradiation of a given fluence degrades all of these cells to the same output. This implies that within lithium concentration variations observed here, the population of radiation produced recombination centers is dependent only on electron fluence and not on lithium concentration. It has been shown that the introduction rate of defects such as the vacancy-phosphorus (E-center) and the majority carrier removal defect in lithium doped silicon are directly related to the phosphorus and lithium concentration respectively. Our experimental evidence would indicate that lithium atoms are

not involved in the structure of the recombination centers. Furthermore, since the effectiveness of the recombination centers is not influenced by total donor concentration in the active area of the cell, the form of the applicable Hall, Shockley, Read equation allows one to conclude then that the energy levels of the center lie relatively deep in the forbidden band. This would indicate that the dominate center in this float zone silicon is not the A-center, but rather the E-center or some other deep lying level. A further experiment involving variation of phosphorus in float zone silicon used for lithium cells would help to support these conclusions.

Two additional studies were performed to investigate the nature of the redegradation and stored at various temperatures. The temperatures used were 25, 35, and 45°C. The cells were irradiated to 3×10^{14} e/cm² prior to storage. Cells in this experiment include some processed from float zone and lopex material. The irradiation and recovery data for 25 and 45°C are shown in Figures 7 and 8. These cells were lithium diffused for 90 minutes and redistributed for 60 minutes at 425°C. Their initial and degraded short circuit currents are intermediate to those with 0 and 120 minutes redistribution on Figure 2. It can also be seen that recovery characteristics also are intermediate to the previously mentioned cells. It is also apparent that, in the case of this data, no significant differences can be observed between cells made from float zone or lopex silicon. Storing the irradiated cells at 45°C produced a strong accelerating effect on the recovery phase. The maximum recovered short circuit current and the pattern of redegradation do not appear to be affected by the increased temperature. The usual pattern of redegradation is apparent within 100 hours after irradiation. The cells shown in Figures 7 and 8 are unusual in that they do not redegrade until after 1000 hours. The lithium diffusion schedule here does not differ greatly from other cells studied and at present no explanation for this effect can be offered. Cell 498 on Figure 8 suffered a severe decrease of short circuit current after 1000 hours storage at 45°C. Coincident to this decrease, the cell showed a catastrophic mechanical failure of the front contact. Therefore, this result is not considered pertinent to redegradation.

At one time we had accumulated some inconclusive data which seemed to indicate that lithium cells irradiated soon after manufacture experienced more redegradation. To further test this hypothesis, a group of lithium cells with a 90-minute diffusion and a 60-minute redistribution at 450°C was split into two subgroups. One group was irradiated within one day after completion of manufacture. The other group was given an identical irradiation three months after manufacture. The data from the irradiation and recovery of these groups is shown in Figures 9 and 10. This data indicates that recovery and redegradation characteristics are not significantly affected by storage before irradiation. It is noted that on the average, the before irradiation short circuit current is slightly higher after manufacture than three months later. If this effect is real, it may be caused by the same physical or chemical changes which produce redegradation. In such a case, redegradation after recovery could be viewed as a continuation or acceleration of this degradation by the irradiation.

In addition to the previously discussed cells diffused at 350 and 425°C, other groups of cells were received for evaluation. Although these cells were not prepared in a particular matrix to facilitate analysis, it is possible to make some interesting observations regarding lithium diffusion and base resistivity variables. A group of float zone silicon cells with a base resistivity of 100 ohm-cm were fabricated by Heliotek with a 500°C lithium diffusion. The data from these cells is shown in Figure 11. The cells were diffused for either 15 or 30 minutes and then redistributed for 30 minutes. The previous work at 425°C has shown that a 15-minute lithium diffusion at 500°C should allow the lithium to reach the junction in very high concentrations. In this case the redistribution should lower the concentration at the junction and make the distribution more uniform. In any event, it is expected that the cell will be heavily doped with lithium. The before irradiation short circuit currents of these cells average 18 ma/cm². This extremely low output is probably due to the high concentration of lithium in the active base region. When the cells are irradiated the short circuit is degraded to about 12 ma/cm². This is very similar to that found in Figure 2 for cells from 20 ohm-cm material, i.e., 5 times more phosphorus. The maximum recovered J_{sc} averages 17.5 ma/cm². The main disadvantage of these cells is their low initial output which also restricts the maximum recovered output. One solution to this problem is to increase the redistribution time. This effect can be seen in the next figure.

Figure 12 summarizes the data for a second group of cells diffused at 500°C. All of these cells except one were made from 20 ohm-cm silicon. It is interesting to note that despite the lower resistivity, the cells with 30-minute diffusion and 30-minute redistribution at 500°C behave nearly identical to the cells in Figure 11. The effect of increasing the redistribution time is shown by cells #461 and 468 in Figure 12. These cells have much higher initial J_{sc} values and also recover to higher values after irradiation. The data on the graph indicates that the donor concentration at the junction dropped significantly after the additional redistribution.

Various diffusions at 400 and 425°C are shown in Figure 13. Most of these cells were made from 100 ohm-cm silicon. Most of these cells are comparable or slightly better than those described in Figure 11. The one exception is cell #317. This diffusion schedule allowed the lithium concentration to be lowered enough to raise the cell output and recovery.

In Figure 14, data from several cells with various resistivities are shown. These cells were diffused in the 400-450°C range and all had in excess of 1×10^{15} Li atoms/cm³ at the junction. As in the case of the cells in Figure 11, the initial J_{sc} and the recovered J_{sc} were relatively low. The lowering of cell output higher lithium concentration occurs uniformly regardless of original resistivity. This is well illustrated by cell #167 which was fabricated from 1500 ohm-cm silicon, but under these diffusion conditions, produced a cell no better than those from 20 ohm-cm material. This effect is again shown in Figure 15. Three cells shown in this figure were lithium diffused at 425°C for 90 minutes. Cell #241, made from 1000 ohm-cm silicon, was not given any redistribution treatment. Cells #305 and 306, made from 20 ohm-cm silicon, were given a 60-minute redistribution at 425°C. Cell #241, despite its initial high purity, has a higher lithium concentration and

subsequently a lower initial and recovered J_{sc} . The 20 ohm-cm cell which was redistributed had much higher initial and recovered J_{sc} values. The lithium concentration at the junction of these two cells is significantly lower than that of cell #241.

A group of cells diffused at the lower temperature of 350°C is analyzed in Figure 16. Two of these cells (389 and 391) were fabricated from 1000 ohm-cm silicon; however, the 30-minute diffusion at 350°C did not allow any detectable lithium to reach the junction. Therefore, most of the active region of the cell was without lithium. As expected, the original and initial degraded J_{sc} of these cells are relatively high. These cells do exhibit some recovery behavior indicating that some lithium has reached the active collection area of the device. The recovery of these devices raises the J_{sc} from about 27 ma/cm^2 to 29 ma/cm^2 . Cell #394, 20 ohm-cm silicon, also is typical of a cell with very little lithium in the active area. Cell #355 is typical of a cell with excessive lithium, it has lower initial and degraded J_{sc} and recovers to only 18 ma/cm^2 . Cell #399 appears to have closer to the optimum lithium concentration. After irradiation, it completely recovers to its initial J_{sc} of 24 ma/cm^2 . It has been apparent in the previous discussions that the output of the unirradiated lithium diffused solar cells are very much dependent upon the amount of lithium diffused into the cells and starting material. This relationship is shown graphically in Figure 17. In this figure the unirradiated short circuit current for a group of Heliotek lithium F.Z. cells is plotted versus the concentration of donor atoms at the junction. It would appear from this data that the initial J_{sc} is a very close function of the donor concentration at the junction. Although there is very little scatter in the data in Figure 17, other observations indicate that it is possible to achieve higher J_{sc} values, in the 10^{14} Li/cm^3 range, than are indicated by this data. Figure 18 is a similar display for a group of Centralab F.Z. cells. Although the variation of J_{sc} and donor concentration at the junction is not as extreme as that in Figure 17, the same trend toward higher J_{sc} in cells with lower lithium concentrations.

In our previous report, we discussed the problem of cells which, after maximum recovery, exhibit a spontaneous decrease in output.³ The cells for which this effect was first reported are still under observation. The most recent observations indicate that the decrease in J_{sc} , for the original group of cells studied, is arrested near that of the initial degraded value of the cells. This data is presented in Figure 19. The concentration of donor atoms at the junctions are also shown on the graph. These concentrations tend to be quite high compared to those of which do not exhibit redegradation. It should be noted the donor concentrations shown on Figure 19 were determined about 9 months after irradiation. A second determination was made approximately 18 months after the irradiation. The results indicated that the donor concentration had decreased by about 50 per cent. This would suggest that the original lithium concentration might have been considerably higher than that shown on Figure 19. If this is the case, the origin of the redegradation effect may be related to very high lithium concentration in the active area of the cell.

Heliotek fabricated two series of lithium cells from quartz crucible material. In one case 200 ohm-cm material was used and in the other case 1 ohm-cm. A lithium diffusion schedule of 90 minutes followed by 30 redistribution at 350°C was used for fabrication. Although these cells recover at room temperature, the time rate is extremely slow. To accelerate this recovery enough to allow practical short time laboratory experiments, the crucible cells were stored at 100°C after irradiation. If one assumes that recovery is a single thermally activated process, the higher recovery temperature should only cause faster recovery. The results of such an irradiation and recovery are shown in Figure 20. The two groups react very differently to irradiation. An electron fluence of 3×10^{14} e/cm² degrades the 1 ohm-cm lithium cell to a short circuit current of 11 ma/cm², but that of the 200 ohm-cm lithium cell is degraded to only 19 ma/cm². The recovery pattern of each type at 100°C is also very different. Both types reach their maximum recovery in about 48 hours at 100°C. The 1 ohm-cm cells recover to a maximum of 19 ma/cm², but the 200 ohm-cm cells recovered to 25 ma/cm². It is very interesting to note that after 3000 hours of 100°C, there is no indication of redegradation in either type of crucible cell.

In Figure 21 the irradiation data is presented for both types of crucible cells. Again the lesser degradation of the 200 ohm-cm cells is readily apparent when compared with the 1 ohm-cm cells. Both types of lithium cells degrade at the rate of 5.5 ma/cm² per decade of electron fluence when tested under tungsten illumination. This rate is significantly lower than the 6.5 ma/cm² per decade of penetrating particle fluence found in standard n/p or p/n solar cells. This lower degradation rate is probably due to annealing of the lithium cells during the irradiation. For comparison purposes, a typical degradation curve for 10 ohm-cm n/p commercial cell is also shown on the graph. The maximum recovered short circuit current values of the 200 ohm-cm lithium cells are represented by the dashed line. It can be seen that these values tend to lie above those of the n/p cells and this trend is stronger as electron fluence increases. To avoid confusion the recovery data for the 1 ohm-cm cells was omitted. Interestingly, the 1 ohm-cm cell irradiated to 3×10^{15} e/cm² did not exhibit any recovery at 100°C during the observation period. Further work is planned to study recovery of these cells from heavy bombardment.

An opportunity to conduct some neutron irradiation experiments on commercial and lithium doped solar cells supplied by Heliotek using the Northrup Triga reactor occurred late in the program. The solar cells tested consisted of six 10 ohm-cm n/p silicon cells and six lithium doped p/n silicon cells. Two cells of each type were irradiated at integrated fluxes of 4.08×10^{11} n/cm², 2.24×10^{12} n/cm² and 1.66×10^{13} n/cm² for $E > 10$ kev. Simultaneously with the neutron irradiation, electron irradiations were conducted at the TRW site on two cells of each group and the remaining cells of each group were kept as controls. The two groups of 10 cells each were provided by Heliotek for this experiment. The measurements that were performed consisted of I-V characteristics and low injection level minority carrier diffusion length.⁵ These measurements were performed prior to irradiation, immediately after irradiation, and as a function of time thereafter to study annealing characteristics. The determination of an injection level dependence was also performed although detailed measurements of the magnitude of the injection level dependence were not performed. The I-V characteristics were obtained under both tungsten and sun simulator environments at approximately one sun intensity.

The degradation of short circuit current versus fast neutron fluence is plotted in Figure 23. The 10 ohm-cm n/p cells responded in a normal manner exhibiting a degradation rate of about 6.5 ma/cm^2 per decade with a critical flux of $1.5 \times 10^{12} \text{ n/cm}^2$ under tungsten illumination. The minority carrier diffusion length for the n/p cells exhibited the correct $-1/2$ degradation slope with a low injection level K value of $2.0 \times 10^7 \text{ n}^{-1}$. These degradation characteristics are considered normal and consistent with previous experiments conducted by both ourselves and others, as presented in the literature. Negligible post irradiation annealing has been observed to date for the n/p cells.

The lithium cells used in this neutron experiment were diffused for 90 minutes and redistributed for 60 minutes at 425°C . The cell material used was n-type, 20 ohm-cm, float zone single crystal silicon. As experienced in electron irradiations the lithium cells were more heavily degraded than the n/p cells, but the degradation rate per decade of neutron fluence (slope) was significantly less, indicating some annealing of damage during irradiation of the lithium cells. The dashed line on Figure 23 represents the maximum recovered short circuit current value of the lithium cells after room temperature storage. It is clearly evident from the data that, after fast neutron fluences in excess of 10^{12} n/cm^2 , the recovered lithium solar cells offer a very significant output advantage over contemporary n/p solar cells.

Figure 24 is a comparative study of room temperature recovery of similar lithium solar cells degraded to the same short circuit current by 1 Mev electrons or fast neutrons. The recovery of the neutron irradiated cells is nearly 10 times slower than that of the electron irradiated cells. The neutron cells, however, recover to a significantly higher output. These differences are probably due to some basic differences in the number and type or relative population of types of radiation produced recombination centers created by the two types of particles.

Commercial non-lithium cells have a close relationship between diffusion length and short circuit current. This relationship is shown as a solid line on Figure 25. We have observed that unirradiated lithium cells typically do not follow this relationship. Data points for several lithium cells are also shown. The data indicates that a lithium cell with a given diffusion length will produce a higher short circuit current than normal cell with the same diffusion length. Other observers have reported enhanced response to red light in lithium cells. Such a red response or an injection level dependence could explain the observations in Figure 25. The failure to follow the previously found relation between J_{sc} and diffusion length is not confined to unirradiated lithium solar cells. The same effect is illustrated in Figure 26 for cells as they are irradiated. In this experiment a group of Heliotek F.Z. cells, lithium diffused at 350°C , were measured for diffusion length before and after various electron irradiations. It can be seen that the change of J_{sc} with irradiation also tends to follow a straight line relationship on this semilog plot. It also appears that the dashed line on Figure 26 falls very close to the central trend of experimental points on Figure 25. This would indicate the added response (enhanced red, injection dependence, or drift field effect) is independent of the nature of the recombination center. This must be true because the relationship holds both for recombination centers

present after the fabrication processing and those produced by irradiation. The two types of recombination centers are different, since only irradiation produced centers react with lithium. Figure 27 is a plot of short circuit current versus diffusion length for two irradiated crucible cells previously described in Figure 21. The higher resistivity cell exhibits enhanced response before, after irradiation and during recovery. The low resistivity cell appears to lose the extra response after irradiation. The full explanation of this effect is desired to aid in the development of more efficient lithium cells.

The present indications are that lithium solar cells will offer considerable radiation hardness when used in very extreme radiation environments. Further work is necessary to determine the relative advantage of float zone or crucible material and the most desirable lithium diffusion schedule.

III. LITHIUM DISTRIBUTION STUDIES

In the previous section, several references were made to the concentration of donors at the junction. These concentrations were determined by capacitance measurements of the solar cells. The nature of the junction diode permits the solution of Poisson's equation, under some conditions, which allows the determination of the dopant concentration on the more lightly doped side of the junction by capacitance measurements. The relationship is as follows

$$N_d = \frac{n V C^2}{q e} \quad (1)$$

The use of this equation requires a determination of the constant n and the internal barrier potential of the junction. In the study of lithium cells we have found considerable variation in the value of n . In addition, the internal barrier potential must be determined by a curve fitting process which is complicated by variations in the constant n . Because of these problems it is desirable to use an expression which eliminates these quantities. For this reason an alternate expression

$$N_d = \frac{C^3}{q e \frac{\Delta C}{\Delta V}} \quad (2)$$

can be derived, which allows a more rapid determination of the donor concentration. In the case of linear graded junctions ($n = 3$), it is desirable to determine the gradient of dopant atom concentration. The expression

$$\frac{dN_d}{dx} = \frac{12 V C^3}{q e^2} \quad (3)$$

allows one to determine this gradient⁶.

In Figure 28 is a plot of capacitance per unit area versus donor concentration for a group of various lithium solar cells. The donor concentration was determined by equation (2). It is apparent that the general trend of data points lies close to the second power relationship of equation (1). The scatter or deviations from this relation are probably due to variations in n and barrier potential between cells with varying lithium diffusion schedules. For this reason all concentration determinations in this report were made by use of equation (2).

In the previous section, it was mentioned that the capacitance-voltage relation for lithium cells could vary between two extremes, a CV^2 relation for cells with little or no lithium at the junction and CV for cells with a high

concentration of lithium at the junction, the lithium being present in the form of a linear concentration gradient. Figure 29 is a plot of capacitance versus voltage for a cell previously discussed in Figure 1. This cell had a relatively low lithium concentration at the junction, and showed good recovery from an electron irradiation of 3×10^{14} e/cm². It can be seen that the unirradiated device is intermediate between a CV² and CV³ relationship. It can be seen that the unirradiated device is very close to CV³ relationship. This behavior is expected in a diffused device; however, in this case it is not the gradient of the boron but the gradient of the lithium as it approaches the junction from the rear of the cell. If the lithium concentration is low compared to the concentration of phosphorus, the cell will exhibit CV² or typical step junction behavior. One effect of the irradiation is to remove lithium from solution in silicon. This can be seen by the decrease of capacitance with irradiation. If enough lithium is removed, the cell will return to CV² behavior. Both effects are illustrated in Figure 29. If a lithium cell exhibits CV² behavior because of too short a lithium diffusion or a heavy irradiation, it will show only marginal or no radiation recovery effect.

Capacitance measurements were used to make a study of the stability of lithium in solar cell after manufacture. Figure 30 is a plot of the lithium concentration at the junction versus time after manufacture. During the first 30 days there is a large increase in concentration which tends to stabilize. Irradiation of 3×10^{14} e/cm² causes a decrease followed by an increase in lithium concentration. An additional effect is caused by storage of these cells at 100°C. At this temperature the concentration of donors near the junction decreases rapidly and stabilizes at the value of the phosphorus concentration. Figure 31 is a similar plot for cells which were irradiated immediately after manufacture. These cells show a very large increase in lithium concentration during the 6 weeks after manufacture and irradiation. The 100°C storage effect is also shown. This data is presented to demonstrate that the lithium concentration at the junction, determined by capacitance, is a very unstable quantity. Therefore, caution must be exercised when using these techniques if a correct analysis of changes in lithium concentration is desired.

The methods of following lithium concentration changes at the junction by capacitance measurements can also be used to follow the changes which occur during the redistribution cycle which can be used following an initial lithium diffusion. All lithium redistributions studied to date have been in the temperature range of 350-500°C. Our experience has shown that it is possible to fabricate a lithium solar cell to completion and then submit the cell to a redistribution cycle. In this way, a cell with good electrical contacts and diode properties can be used as a test vehicle for the study of lithium movements. To date, we have only completed these experiments at 250°C. This temperature was selected because significant lithium diffusion could be accomplished in times of a few hours and no thermal damage to the cells. A lithium diffusion which requires 1 hour at 350°C would require about 10 hours at 250°C. By reducing the temperature this amount, the redistribution of lithium can be slowed to permit closer observation. Our studies of lithium cells have shown that redistribution can significantly improve the recovery characteristics in many cases. Thus, studies of redistribution at lower temperatures may allow a better optimization of the cell parameters.

The cells fabricated by Heliotek included a group which were lithium diffused for 30 minutes at 350°C. The evaluation of these cells indicated that no detectable quantities of lithium had reached the junction. It was also noted that these cells (see Figure 4, cells 1633 and 1634) did not recover from the degraded condition after irradiation. These observations indicate that the diffusion front of lithium atoms has not reached the active region of the device. For this reason these cells were selected for a study of changes in donor concentration at the junction during redistribution. Several cells from this group heated to 250°C for various periods of time to allow redistribution of lithium. The treatment was periodically interrupted to permit electrical measurements. The results of the capacitance measurements are shown in terms of donor concentration at the junction versus time at 250°C in Figure 32. Since the original cell material was 20 ohm-cm, n-type silicon, the original donor concentration appears to reflect the normal scatter of phosphorus concentration in this material. Although the donor concentration changes only slightly with 2 hours, it begins to rise very abruptly by 4 hours. Between 10 to 18 hours at 250°C the donor concentration reaches a maximum and declines at a relatively slow rate. In this case, the maximum appears to be roughly $4.5 \times 10^{15} \text{ cm}^{-3}$. Since the original phosphorus concentration was $2.5 \times 10^{15} \text{ cm}^{-3}$, this redistribution can raise the lithium concentration at the junction roughly to that of the phosphorus.

An alternate analysis of the capacitance measurements is shown in Figure 33. This is a plot of capacitance versus potential. The potential is the sum of the applied bias and the internal barrier potential. The initial measurements indicate CV^2 behavior which is typical of an abrupt boron diffused junction in phosphorus doped silicon. This situation is unchanged by 2 hours at 250°C. After 4 hours the slope of the C-V relation started to decrease indicating a trend toward a $CV^3 = k$ relation or, linear lithium gradient junction. This trend continues to a minimum slope, and thereafter the slope increases slowly. When the redistribution of this cell was terminated at 48 hours the slope is $-1/2.3$ and rapidly approaching $-1/2$. Thus, this C-V data confirms the model previously suggested from Figure 32.

When the redistribution of the previously mentioned cells was interrupted for capacitance measurements, it was possible to determine the short circuit current of the devices. This permitted a continuous study of the effects of redistribution on cell output. This data is shown in Figure 34. The data in this figure indicates the redistribution decreases the J_{sc} roughly linearly during the first 12 hours. The maximum decrease is roughly 10 percent. The decrease is less than the variation of J_{sc} among as manufactured cells in this group. Further redistribution time does not appear to change the short circuit current. The next logical step in this series of experiments would be evaluations of the irradiation recovery at various stages of the redistribution. This work is in progress at the time of this report. An evaluation of the recovery of cell #1902 after a 48 hour redistribution at 250°C is shown in Figure 35. The cell is interesting in that it recovers to a J_{sc} of 28 ma/cm^2 after an irradiation of $3 \times 10^{14} \text{ e/cm}^2$. The effects of this irradiation on the C-V relation can be seen in Figure 33. Apparently the irradiation removed a considerable quantity of donors at the junction.

Further evaluations are necessary before any conclusions can be drawn; however, the lower temperature lithium redistribution done "in vivo" offer an opportunity to closely study all the factors involved in the optimization of recovery properties to make a superior lithium solar cell.

IV. RECOVERY KINETICS STUDIES

The most important problem relating to the study of lithium solar cells is the determination of the solid state reaction which is responsible for the recovery from the irradiated condition. Despite the study devoted to this problem, only limited information is known regarding the nature of the recombination centers and the role of lithium in the recovery process. It is known that lithium diffusion is the kinetic limiting step in the process; however, much more knowledge is needed to construct a theoretical model. The basic information necessary for the model is:

1. The kinetically limiting process
2. The form or order of the recovery kinetics
3. The identity of the reacting species

If the theoretical model is to be accepted it must explain the following observed effects or phenomena:

1. The room temperature annealing of radiation produced recombination centers.
2. The annealing rate reducing effect of oxygen
3. Increased lithium concentrations increase the annealing rate
4. Increased irradiation decreases the annealing rate of lithium solar cells.
5. Excessive irradiation will exhaust the annealing effect
6. The annealing is not always complete
7. Recombination centers present after manufacture are not removed by lithium
8. Some cells, heavily doped with lithium, regrade after recovery
9. The form or order of the recovery kinetics appears to be sensitive to the lithium concentration.

The theory of solid state reaction kinetics often requires new treatments in addition to those of classical chemical kinetics. These treatments are necessary because of factors peculiar to the solid state such as diffusion limited processes and inhomogeneous distributions. Some of the mathematical forms which have been applied to solid state reactions are shown in Figure 36. Our initial effort in the recovery kinetics problem indicated that second order behavior would describe the recovery. This data was obtained from study of recovery in lithium doped gold barrier diodes. These results are shown in Figure 37. Although the data appears to fit the second order relation,

some reservations are necessary. The time constant for room temperature recovery is independent of the fluence of electron, i.e., initial concentration of recombination centers. This situation is more typical of a first order reaction rather than second order reaction. Also, it can be seen from Figure 36 that during the first one-third of the reaction, the difference between first and second order kinetics is small. Therefore, a critical determination between the two forms should emphasize the last half of the reaction. The form of second order equation used here is suitable only for a reaction involving two species having equal concentrations. If this condition is applied generally, it places a severe limitation on the development of a theoretical model for the reaction.

A general theoretical treatment of kinetics of diffusion limited reactions has been proposed by Waite. In this treatment, Waite gives a detailed solution for the reaction of two species which are uniformly distributed. The essentials of Waite's theory for such a case are:

1. An initial transient will appear in the case of species which diffuse slowly and have a small capture radius.
2. If the concentrations of both reacting species are equal the reaction will be second order after the transient.
3. If the concentration of one reacting species is much greater than the other, the reaction will be first order after the transient.
4. The time constant of the exponential (first order) is inversely proportional to the concentration of the more populous of the two reacting species.

Our knowledge of the diffusion constant of lithium and reasonable estimate of the capture radius indicate that the transient which Waite predicts should dominate the kinetics for too short a period of time for experimental observation. This, of course, assumes that the recovery is the reaction of a lithium atom with a recombination center. The range of 1 Mev electron fluence in which we have experimented is from 10^{13} to 10^{16} e/cm². The introduction rate of known recombination centers for such radiation is very roughly 0.1 cm⁻¹. Thus, the range of recombination center concentration would vary between 10^{12} to 10^{15} cm⁻³. The range of lithium concentration encountered in lithium solar cells is difficult to define because of the extremely nonuniform distribution of lithium. Determination of the lithium concentration at the junction by capacitance is of no direct help in determining the typical concentration in the active area of a cell. Since the linear lithium gradient is found to be in excess of 10^{19} cm⁻³, the lithium concentration increases by 10^{15} cm³ for each micron distance from the junction. The work done by the Heliotek group indicates that the linear increase does not continue to any great depth in the cell, but that the lithium concentration in the active area of the device will be between 10^{16} and 10^{17} cm⁻³.⁸ If the assumptions hold, the lithium concentrations will always be at least an order of magnitude greater than that of the recombination centers. Under such conditions the recovery kinetic should exhibit a first order dependence.

Our experimental studies of recovery kinetics are done through determination of minority carrier diffusion lengths of irradiated lithium solar cell and lithium doped silicon gold barrier diodes.⁵ Since the concentration of recombination centers is inversely proportional to the square of the minority carrier diffusion length, it is easy to develop an expression for the unannealed fraction of radiation produced recombination centers. This parameter, recorded as a function of time, permits close monitoring of the recovery.

The previous work on recovery of gold barrier diodes was done on float zone silicon. Lithium doped quartz crucible silicon was fabricated into gold barrier diodes for recovery study. The lithium concentration of this silicon was $1.8 \times 10^{16} \text{ cm}^{-3}$. Because of the slow room temperature recovery in quartz crucible silicon, these devices were allowed to recover from the irradiated state at 100°C . The results of this work are shown in Figure 38. One diode was irradiated with 10^{13} e/cm^2 , the other with 10^{14} e/cm^2 . The annealing proceeded faster than expected and very few data points were obtained. Although there is scatter in the data, the trend appears to follow the exponential function. Since most of the data was taken during the anneal of the last half of the defects, it is more useful in a determination of first order over second order kinetics. This interpretation conflicts with that originally given to the data in Figure 37. The earlier data was concentrated on the early half of the annealing cycle. One similarity between both sets of data is the independence of the time constant with electron fluence. This new data is not conclusive enough to supplant the original conclusion; however, it is sufficient reason to withdraw the original conclusion regarding second order kinetics and re-examine the problem experimentally.

Additional work was done on the kinetics problem using lithium solar cells. The possible inhomogeneity of the lithium concentration in cells can be a complicating factor if the concentration of lithium is a variable in the kinetics. Of the cells studied, a large fraction have produced interesting data which can be analyzed. An example of this behavior can be seen in Figure 39. In this experiment a lithium cell (30-minute diffusion at 350°C , 120-minute redistribution) was irradiated with 10^{14} e/cm^2 . The electron fluence was deliberately kept low to insure that the lithium concentration was large compared to that of the radiation produced recombination centers. The diffusion length of this cell was degraded from 44 microns to 14.2 microns. The recovery was monitored by diffusion length measurements and converted into unannealed fraction in the manner used for gold barrier diodes. The unannealed fraction is shown to have an excellent fit to an exponential function of time as required for first order kinetics. Unfortunately, the experiment was discontinued when 25 percent of the defects still remained. Despite this fact, there is no possibility of fitting these points to a second order relation.

As previously mentioned, to make conclusive fit of data to the first order relation (exponential) it is best to concentrate the data in the last two-thirds of the recovery, because of the mathematical similarity to the second order function during the first third of the recovery. For this reason,

the data in Figure 40 is of particular interest. The experimental details are the same as in Figure 39, except that the cell was lithium diffused for 90 minutes at 350°C with no redistribution. The concentration of lithium at junction is nearly the same in this cell as that in the previous figure. In this case the experiment was continued until less than 2 percent of the radiation defects remained. As can be seen on the figure, the data points closely follow the exponential relation throughout the observation period. Although the concentration of lithium at the junction is nearly the same for cells 1660 and 1627, the latter cell has an exponential decay constant which is smaller by a factor of four. If Waite's theory is assumed to be valid, this would indicate a four times higher lithium concentration in the active area of the device. This relation of lithium concentration to recovery constant could not be confirmed at this time, but should be considered in future work as a critical test of Waite's theory and the simple model of a lithium atom reacting with a recombination center.

An additional experiment was conducted to study the effect of increases in the electron fluence upon the recovery. To facilitate this study, two cells, which were lithium diffused for 30 minutes at 350°C, were given a redistribution treatment for 18 hours at 250°C. It was hoped that this treatment would give the same uniform lithium concentration in each of the cells. The data in Figures 41 and 42 indicate that the lithium concentration at the junction of cell 1902 is 50 percent greater than that of cell 1635. The data points in both figures appear to follow an exponential decay up to the last 10 percent of the recovery. The recovery time constants in both cases (4 and 10 hours) are considerably longer than those in Figures 39 and 40 (90 and 23 minutes). The recovery time constants do not appear to bear any relation to the concentration of lithium at the junction for the 10^{14} e/cm² irradiations. The increase of electron fluence from 10^{14} to 10^{15} e/cm² appears to have caused an increase in the recovery time constant. Capacitance measurements on cell 1902 after irradiation indicated that the concentration of donors at the junction was reduced to below half the pre-irradiation value. It is reasonable to suppose that the increased recovery time required after increased fluence is due to the removal of lithium associated with radiation damage other than recombination. Further study is necessary to clarify the increase of recovery time with electron fluence.

Not all lithium solar cells will recover in an exponential form that directly suggests first order kinetics. The cells which we have examined tend to be lower in lithium concentration at the junction compared to other studies. Some cells which we have studied appear to recover in a form which suggests a combination of two or more exponentials. Examples of this behavior are shown in Figure 43. Such behavior may be caused by regions of high lithium concentration recovering quickly during the initial period, while regions of lower lithium concentration limit the latter stages of recovery with a slower time constant. These cells also have higher concentration of lithium at the junction than those previously mentioned in recovery studies. Both cells have N_j values of 8×10^{14} cm⁻³.

V. OTHER IMPURITY STUDIES

The use of lithium to promote the room temperature annealing of radiation damage was the second successful attempt of many to use impurities to reduce radiation damage in solar cells. The substitution of boron doped p-type silicon for phosphorus doped n-type had previously achieved a considerable increase in radiation resistance. There is still need to improve solar cell radiation hardness. With this interest in mind, experiments were conducted to evaluate the effects of electron irradiation on silicon with various impurities.

An origin of radiation damage lies in the fact that atoms are displaced from their lattice sites and these vacant sites move through the crystal until they are trapped by impurities to form recombination centers. One possible method of reducing the damage is to trap the vacancies and immobilize them before they can form recombination centers. One method to trap vacancy is to allow it to enter the compressive strain field which surrounds an oversize atom dissolved in the host lattice. One choice for the oversize atom to use in silicon is germanium. Germanium will dissolve in large concentrations and still permit single crystal growth. Germanium is believed to be electrically inactive in silicon and approximately 5 percent larger in this type of lattice.

For these reasons, a single crystal of p-type boron doped silicon-13 percent germanium alloy was grown by Wacker Chemical Corp. of Los Angeles. The crystal was grown by the quartz crucible method and had a resistivity of 8 ohm-cm. Some of this material was fabricated into n/p solar cells by Peter Iles of Centralab Semiconductor. It was possible to fabricate excellent cells from this material. The irradiation data for these cells is shown in Figure 44. The short circuit current was monitored while the 1 Mev electron fluence was increased. The critical fluence for these cells was 3×10^{14} e/cm². Thus, the Si-Ge alloy cells are somewhat less radiation resistant than the standard 10 ohm-cm n/p silicon cell, but considerably more resistant than the p/n solar cell. The effect of the germanium was opposite to the expected action. The presence of this high concentration of germanium atoms enhanced the production recombination centers.

A bismuth doped silicon crystal was grown by the quartz crucible method. The resistivity of this crystal was 0.4 ohm-cm. The material was fabricated into gold barrier diodes. It was possible to irradiate these devices and monitor the radiation damage by diffusion length measurements. The results of the irradiation are shown in Figure 45. The bismuth doped silicon appears to be more susceptible to damage than 1 ohm-cm p/n solar cells. This is in part due to the increased majority concentration, which has the effect of decreasing the lifetime or diffusion length, according to the applicable statistical equations. The substitution of bismuth for phosphorus does not appear to offer any advantage in regard to radiation damage.

The interest in lithium doping to achieve radiation resistance has raised inquiries as to the effect of sodium doping. Some reports have indicated that sodium also will act as a donor in silicon.⁹ A sodium doped silicon crystal was quartz crucible grown by Wacker Chemical Corp. for irradiation analysis. Immediately after solidification, this crystal was n-type with a resistivity of about 1 ohm-cm. Within a month after manufacture the resistivity of the crystal had increased to 100 ohm-cm. The results of an atomic absorption spectroscopic analysis indicate 12 p.p.m. sodium in the crystal. It must be concluded that although the crystal contained in excess of 10^{17} Na atoms/cm³, the sodium was electrically inactive or in a second phase. This material was fabricated into gold barrier diodes. These diodes were irradiated to an electron fluence of 10^{14} e/cm². This reduced the minority carrier diffusion length to 73 microns. After 45 days at room temperature the diffusion length was 86 microns. An additional 24 hours at 100°C did not change this value. It was concluded that the sodium had little or no effect in increasing the radiation resistance of the material. The high resistivity was probably the reason for the improvement relative to 1 ohm-cm p/n cells shown on Figure 45.

VI. SUMMARY

The studies reported in this report were intended to gather as much information as possible relating to radiation resistance of lithium solar cells. The nature of the manufacture of lithium cells allows wide latitude in their properties. For this reason considerable effort is required to determine the most desirable method of manufacture of lithium solar cells for a radiation environment. The best lithium cells tested appear to be only marginally better than n/p solar cells under electron bombardment. In a fast neutron environment, however, the lithium cell is clearly superior to any other available solar cells. The following criteria for selection of lithium solar cells are valid.

1. Excessively high lithium concentrations lower cell output to undesirable levels
2. Extremely low lithium concentrations do not produce a detectable room temperature annealing effect
3. Higher resistivity starting materials produce lithium solar cells which are superior because of less initial degradation and higher maximum recovery.
4. The oxygen concentrations found in quartz crucible silicon have the effect of greatly slowing the recovery.

The distribution of lithium within the cells is found to be extremely non-uniform. In the extreme cases the concentration of lithium increases linearly with distance away from the junction. Capacitance measurements are used to determine donor concentrations near the junction. This method was used to monitor the increases in lithium concentration at the junction after manufacture and irradiation of lithium cells. It was also used to detect the changes in lithium concentration caused by storage at 100°C and a complete redistribution cycle at 250°C.

The previously reported conclusions on the kinetics of recovery were not supported and considerable evidence was presented to indicate that the recovery reaction obeys first order kinetics when the lithium concentration is much greater than the radiation produced recombination center concentration.

The radiation resistance of bismuth doped silicon, sodium doped silicon, and a boron doped silicon-germanium alloy was investigated. In all cases, these materials did not offer an advantage over presently used materials.

TABLE I. Lithium Cell Data

Diffusion Temperature, Time, Time Redistribution	Typical Donor Con- centration at Junction (C_m^{-3})	Typical Lithium Con- centration at Junction (C_n^{-3})	CV^n	Lithium Concentra- tion Gradient (C_m^{-4})	Half Recovery Time (Hrs.) $3 \times 10^{14} \text{ e/cm}^2$ $3 \times 10^{15} \text{ e/cm}^2$
350°C, 5 min, 0 min	2.7×10^{14}		CV^2		
350°C, 5 min, 60 min	2.8×10^{14}		CV^2		1000
350°C, 5 min, 120 min	2.6×10^{14}		CV^2		500
350°C, 30 min, 0 min	2.8×10^{14}		CV^2		
350°C, 30 min, 60 min	3.4×10^{14}	0.9×10^{14}	$CV^{2.5}$		50
350°C, 30 min, 120 min	6.7×10^{14}	4.2×10^{14}	CV^3	1.9×10^{19}	10
350°C, 90 min, 0 min	5.6×10^{14}	3.1×10^{14}	$CV^{2.8}$		10
350°C, 90 min, 60 min	7.8×10^{14}	5.3×10^{14}	CV^3	2.8×10^{19}	3
350°C, 90 min, 120 min	7.1×10^{14}	4.6×10^{14}	CV^3	1.4×10^{19}	5
425°C, 5 min, 0 min	2.7×10^{14}		CV^2		∞
425°C, 5 min, 60 min	3.3×10^{14}	0.8×10^{14}	$CV^{2.5}$		10
425°C, 5 min, 120 min	3.5×10^{14}	1.0×10^{14}	$CV^{2.8}$		20
425°C, 30 min, 0 min	6.5×10^{14}	4.0×10^{14}	CV^3	2.6×10^{19}	
425°C, 30 min, 60 min	8.0×10^{14}	5.5×10^{14}	CV^3	2.6×10^{19}	3
425°C, 30 min, 120 min	4.0×10^{14}	1.5×10^{14}	CV^3	1.4×10^{19}	10
425°C, 90 min, 0 min	1.5×10^{15}	1.2×10^{15}	CV^3	6.9×10^{19}	1
425°C, 90 min, 60 min	8.0×10^{14}	5.5×10^{14}	CV^3	3.0×10^{19}	2
425°C, 90 min, 120 min	6.9×10^{14}	3.5×10^{14}	CV^3	1.4×10^{19}	3

TABLE I.

LITHIUM CELL DATA

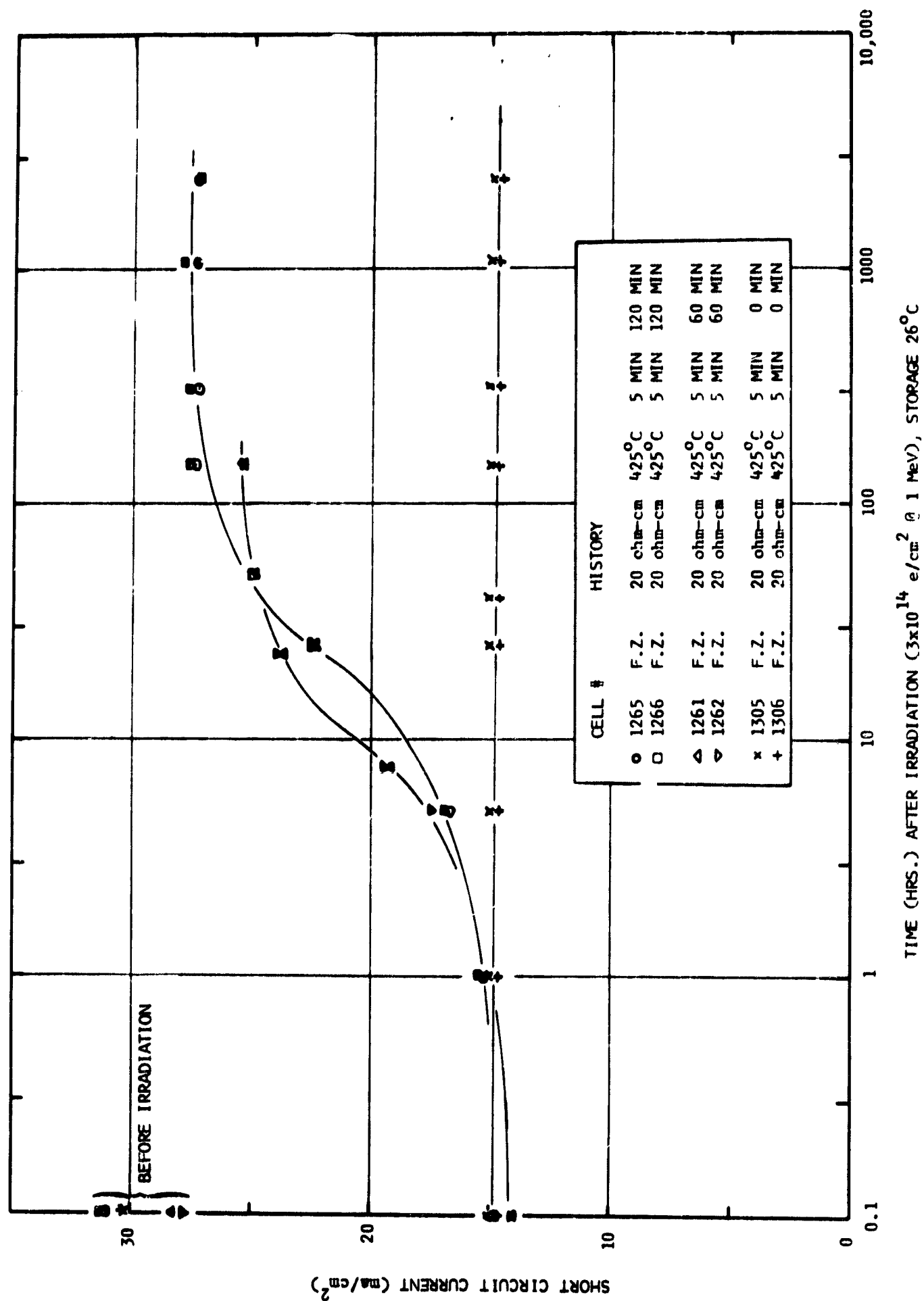


FIGURE 1. RECOVERY OF SHORT CIRCUIT CURRENT OF
IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

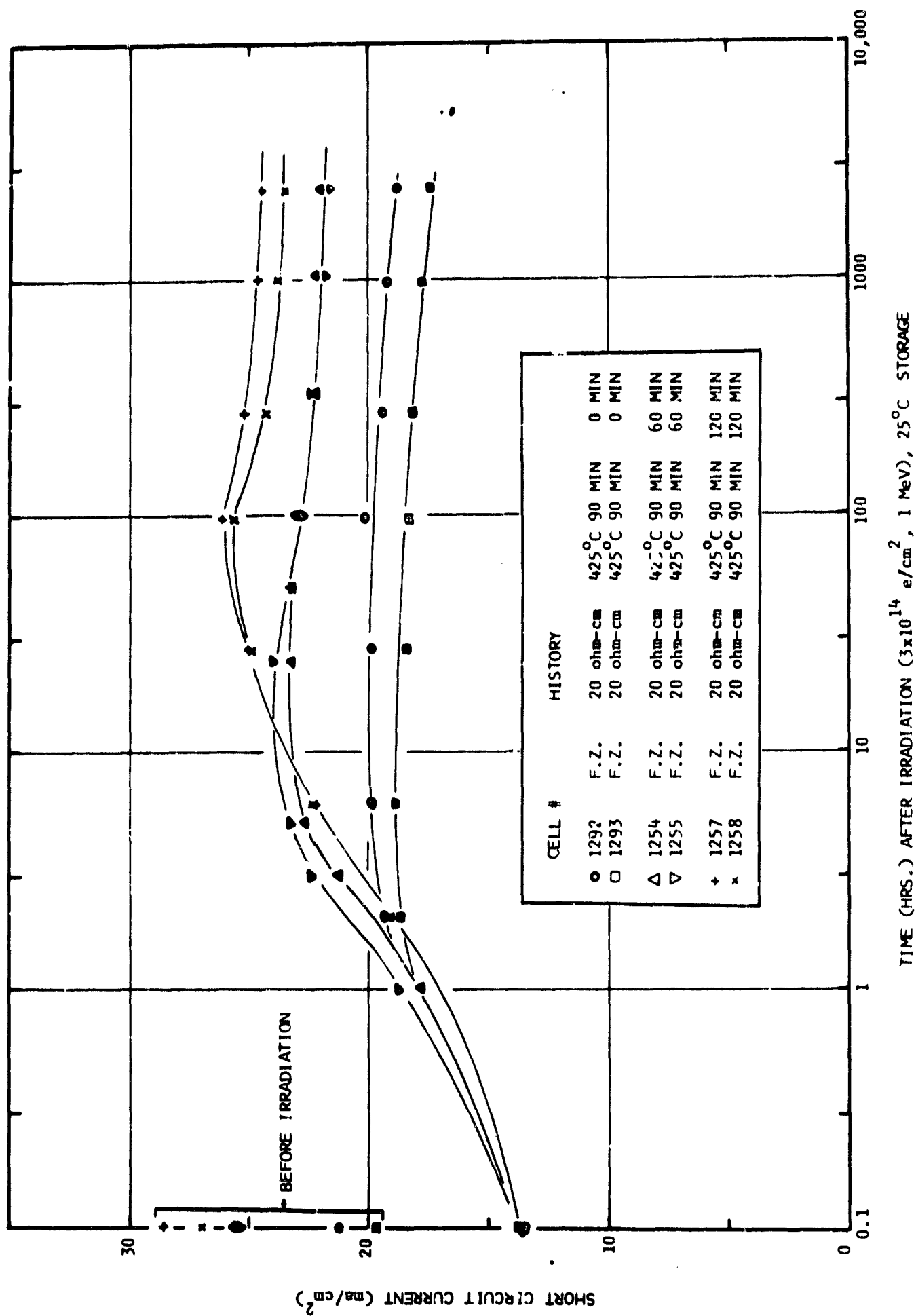


FIGURE 2. RECOVERY OF SHORT CIRCUIT CURRENT OF
IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

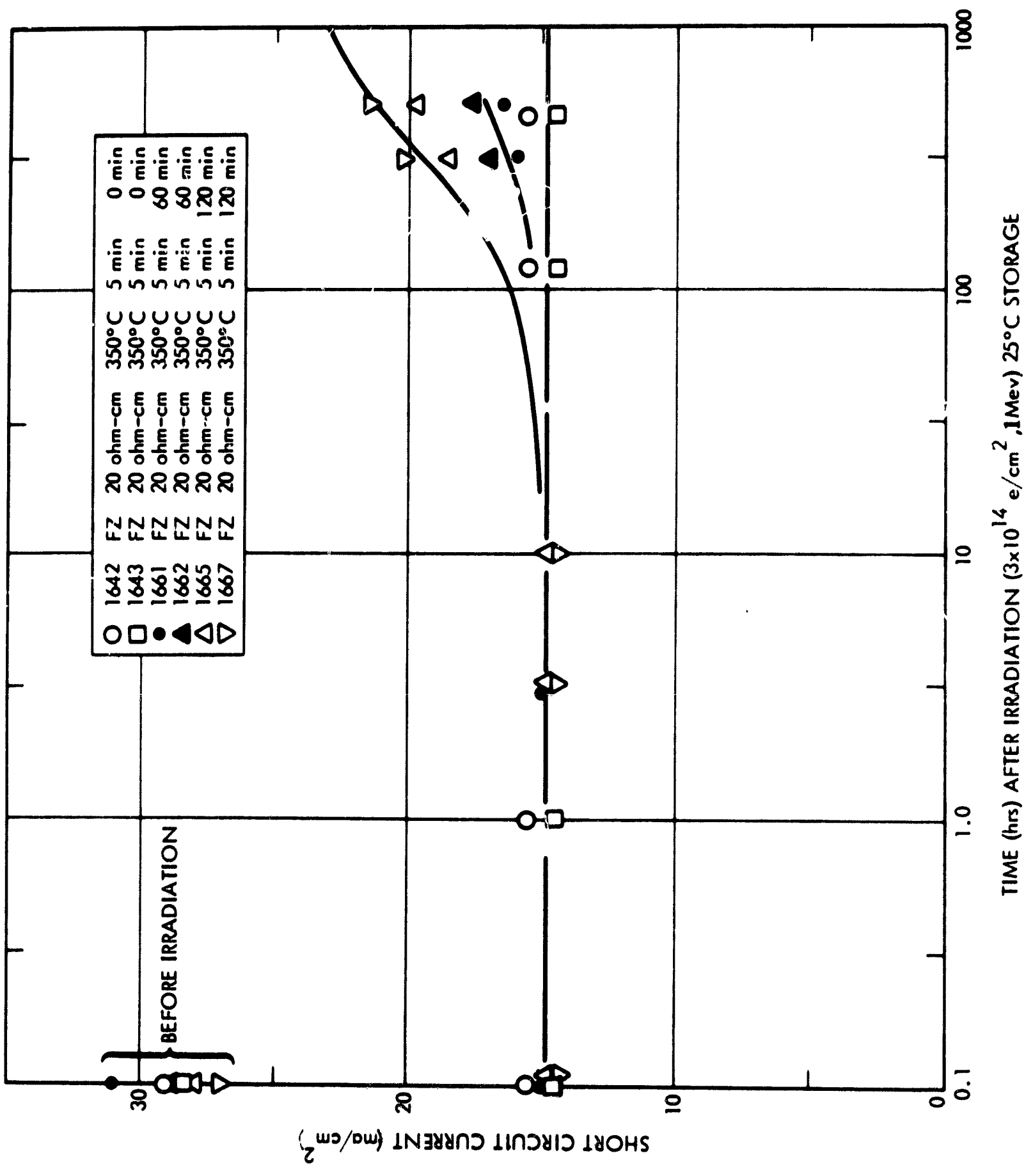


FIGURE 3. RECOVERY OF SHORT CIRCUIT CURRENT OF
IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

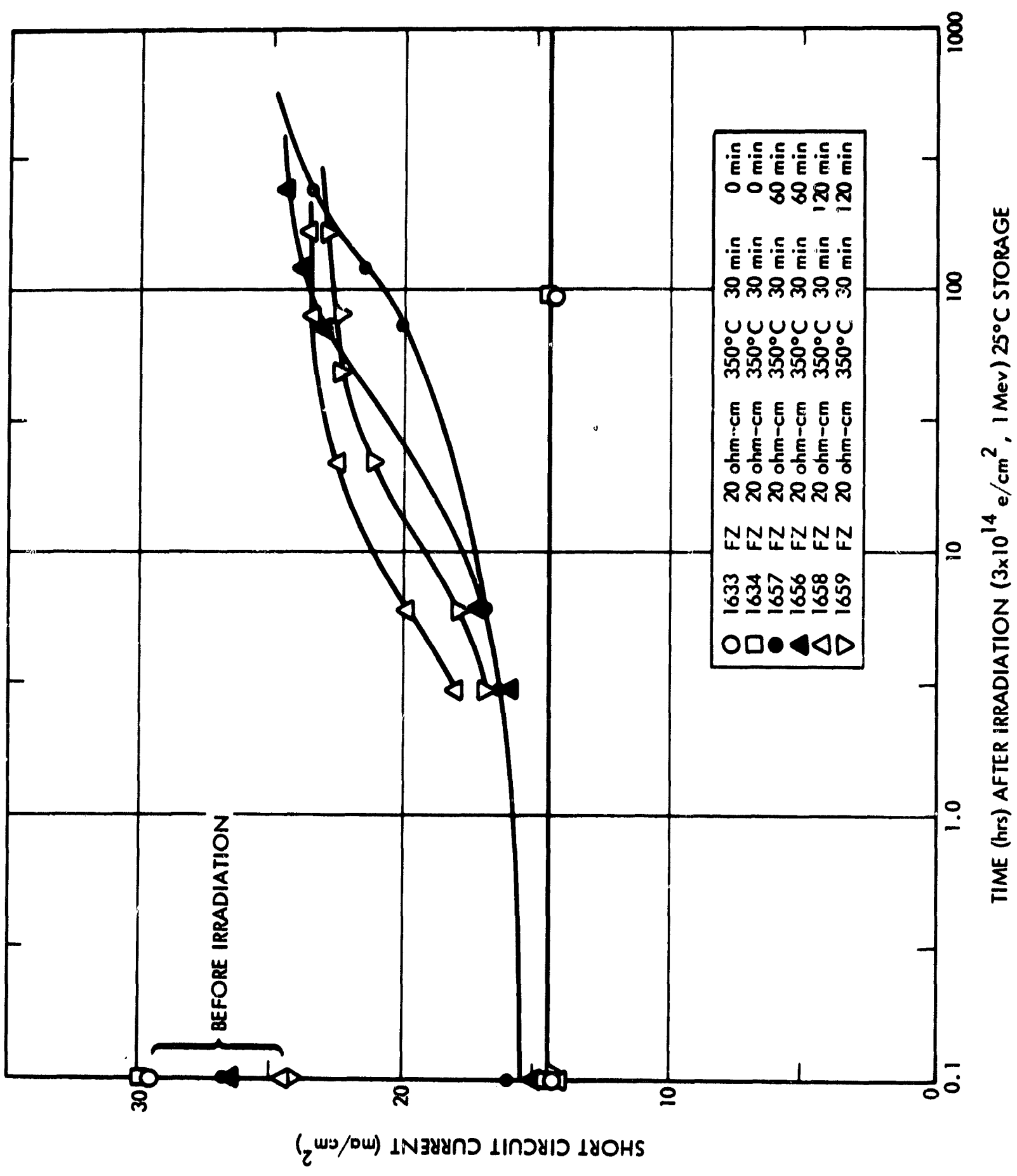


FIGURE 4. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

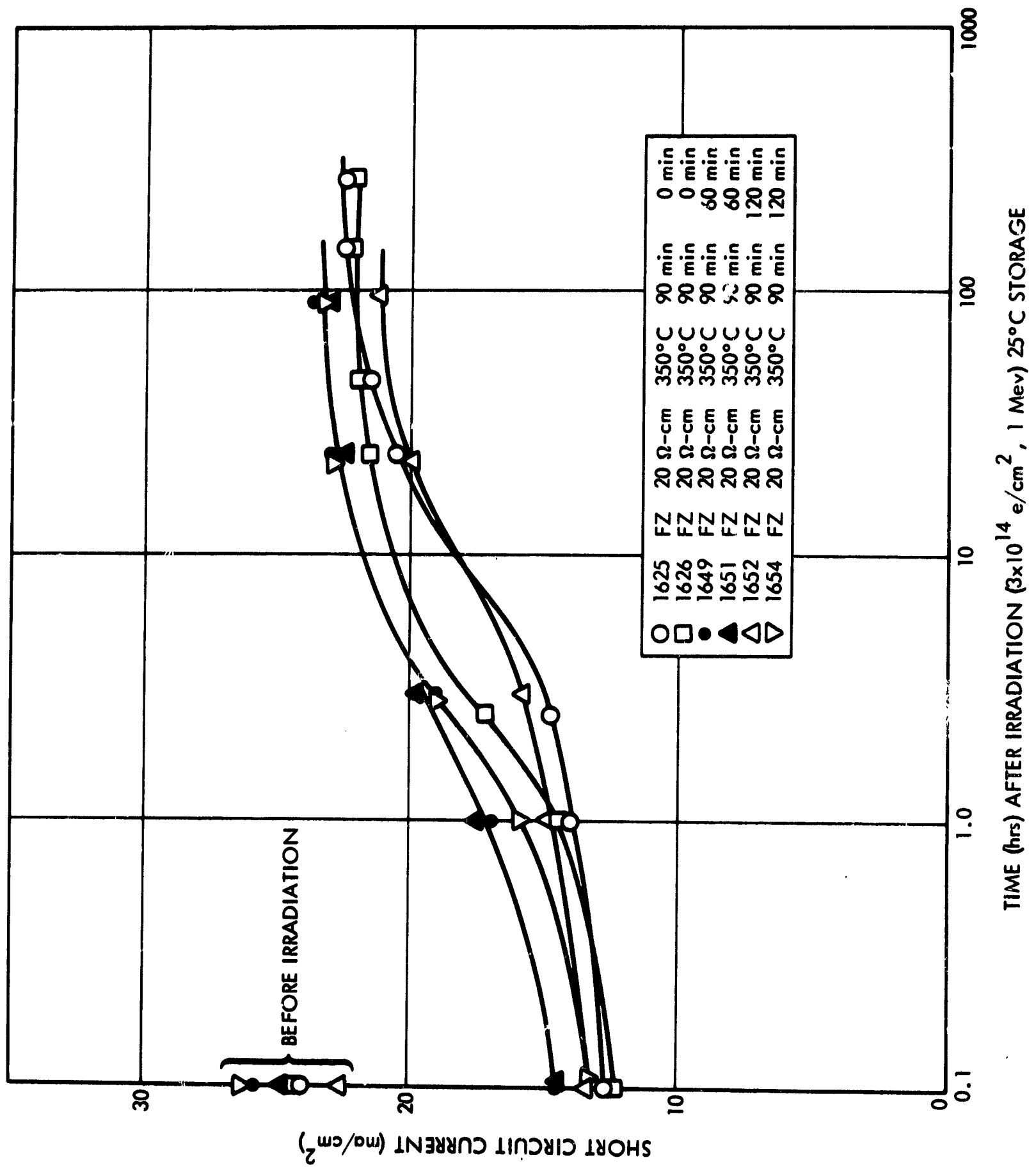


FIGURE 5. RECOVERY OF SHORT CIRCUIT CURRENT OF
IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

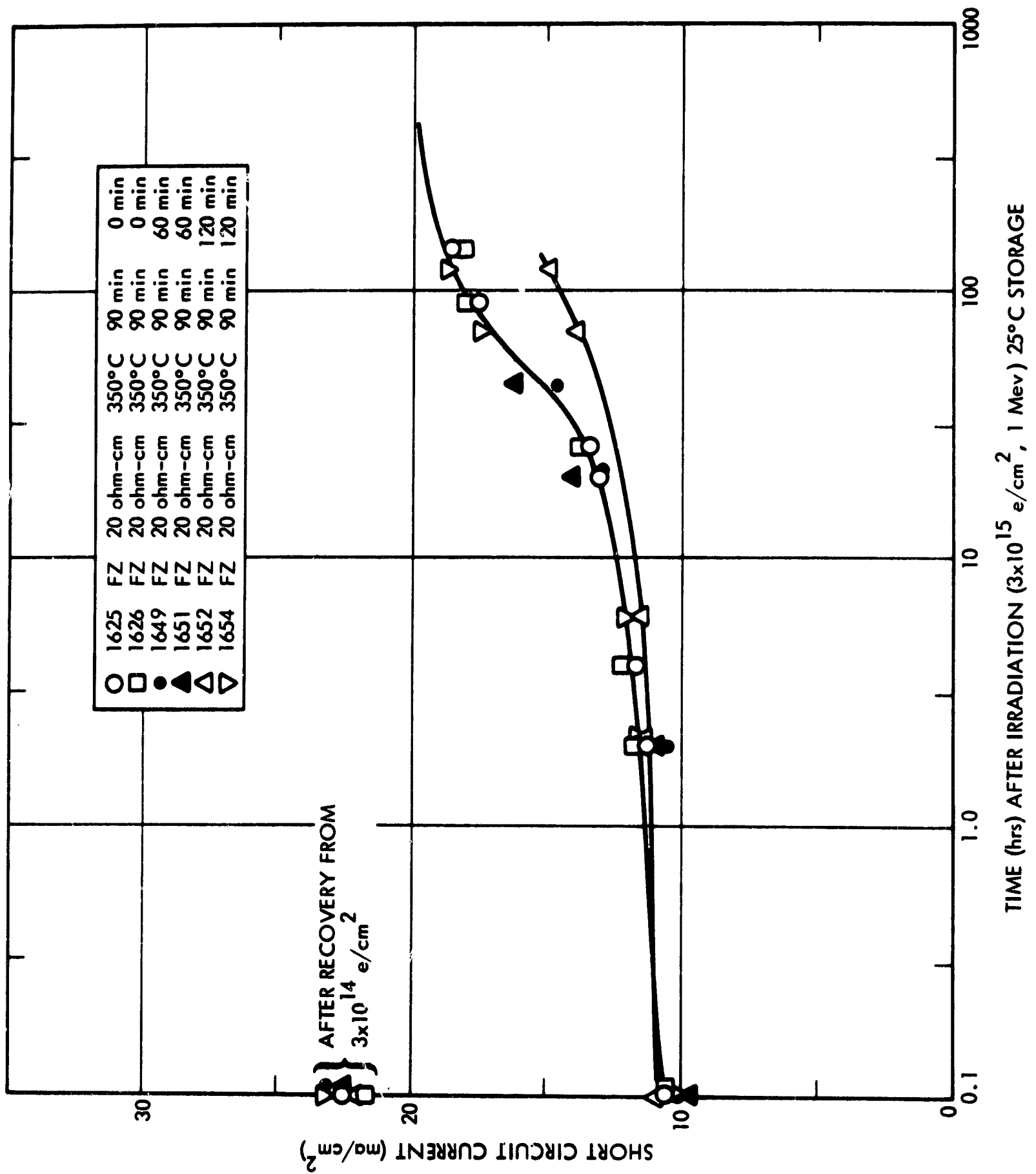


FIGURE 6. RECOVERY OF SHORT CIRCUIT CURRENT OF
IRRADIATED HELIOTEK LITHIUM SOLAR CELLS

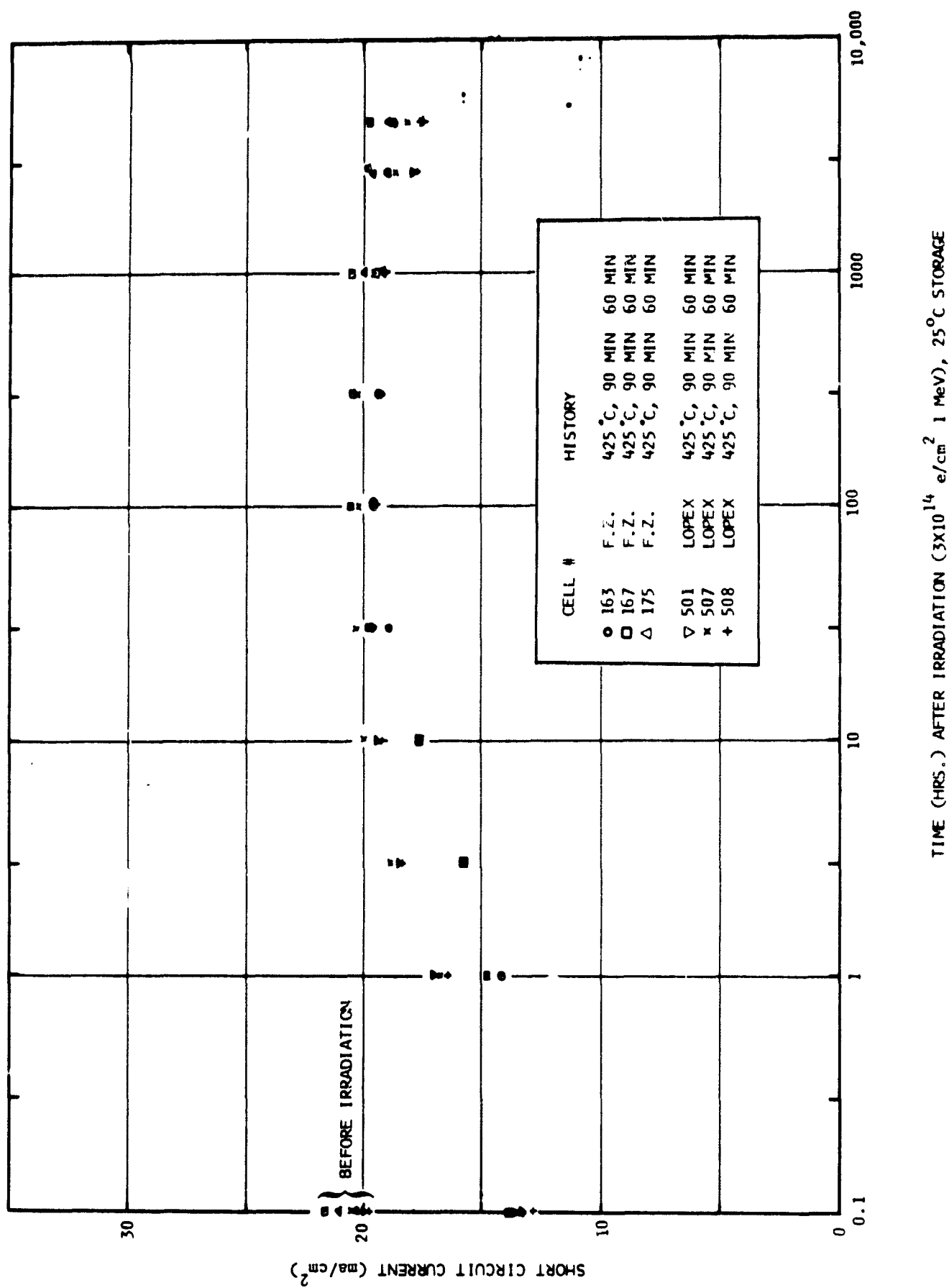


FIGURE 7. EFFECT OF STORAGE TEMPERATURE ON RECOVERY, 25°C

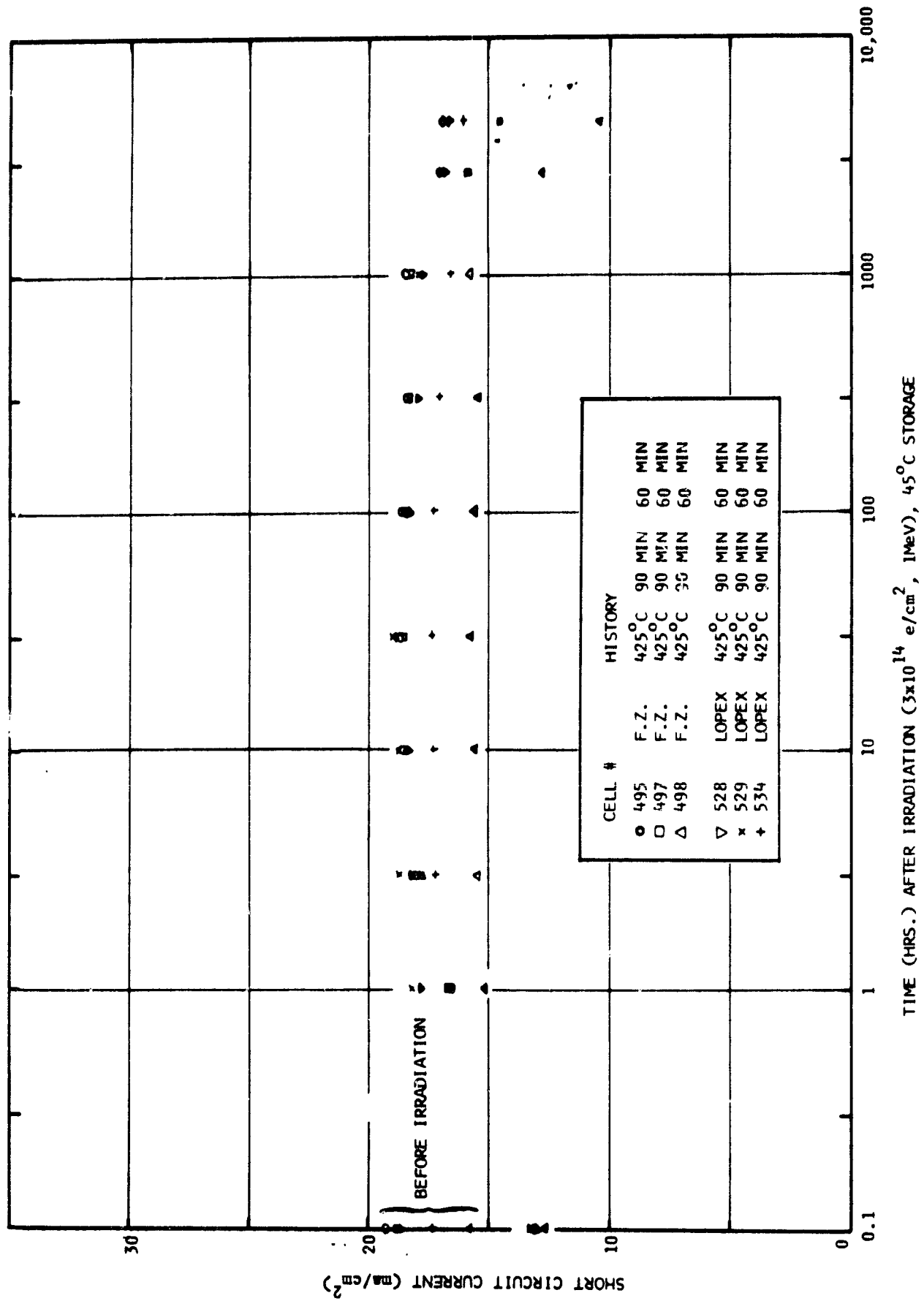


FIGURE 8. EFFECT OF STORAGE TEMPERATURE ON RECOVERY, 45°C

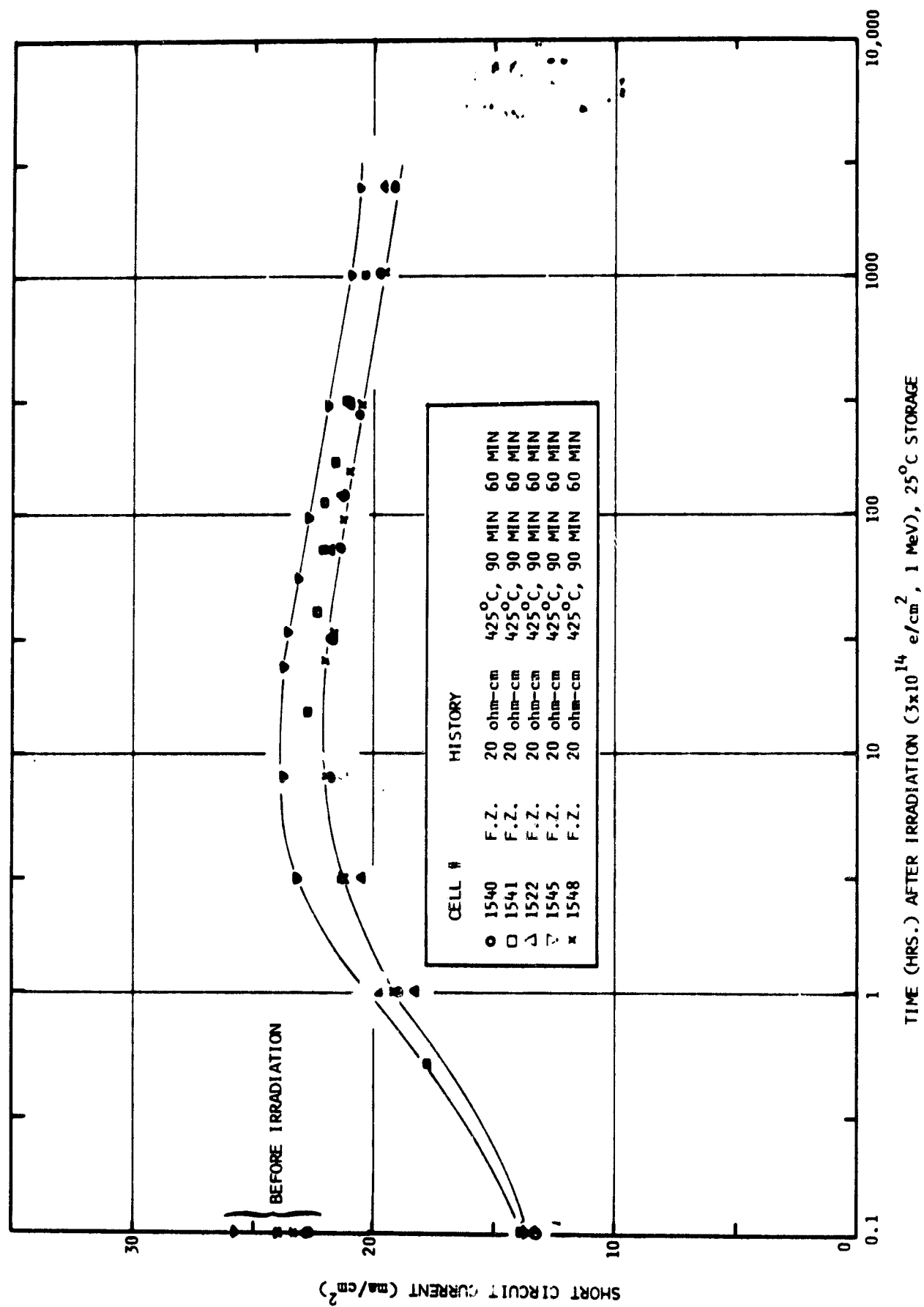


FIGURE 9. EFFECT OF IRRADIATION IMMEDIATELY AFTER MANUFACTURE

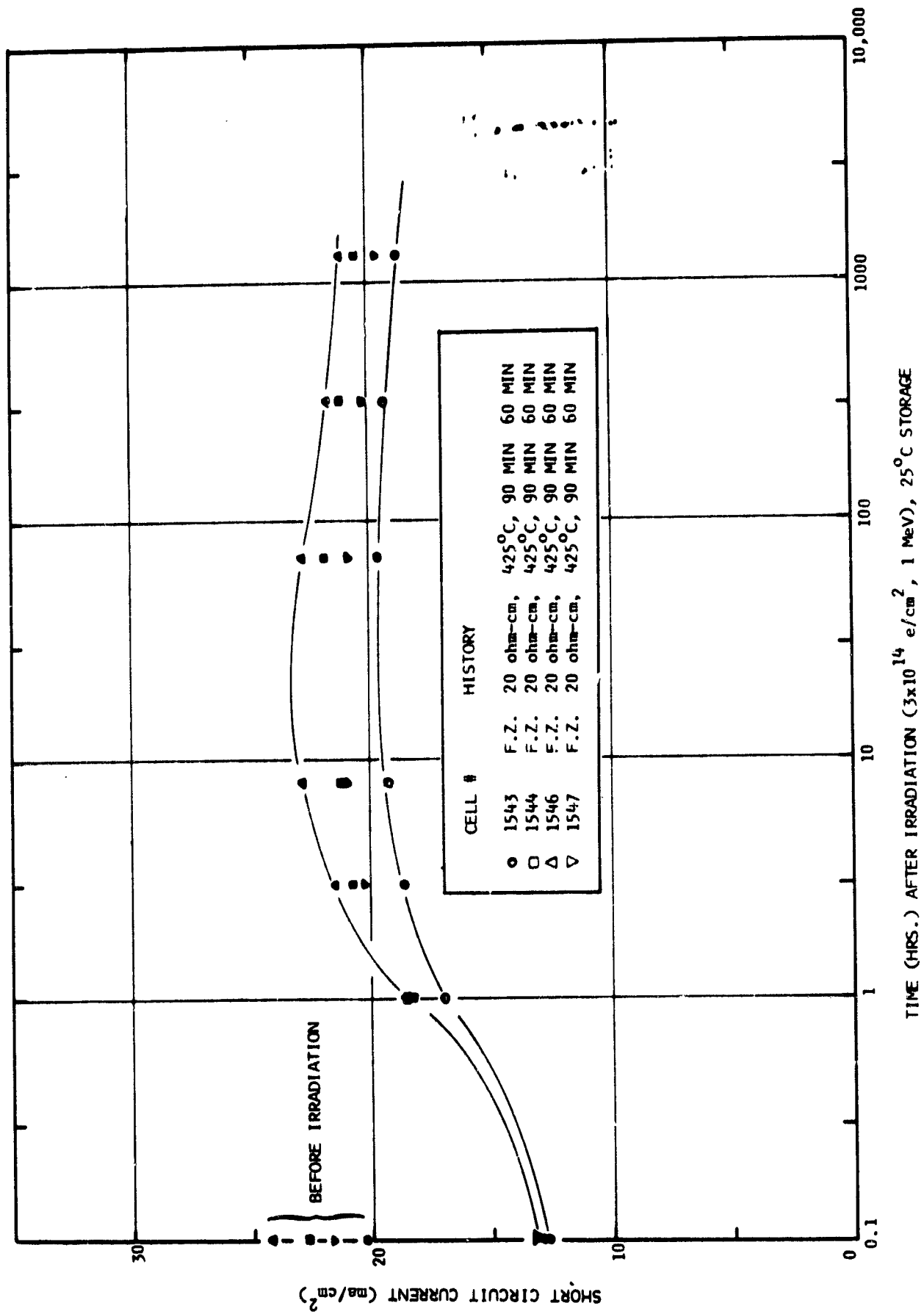


FIGURE 10. EFFECT OF IRRADIATION THREE MONTHS AFTER MANUFACTURE

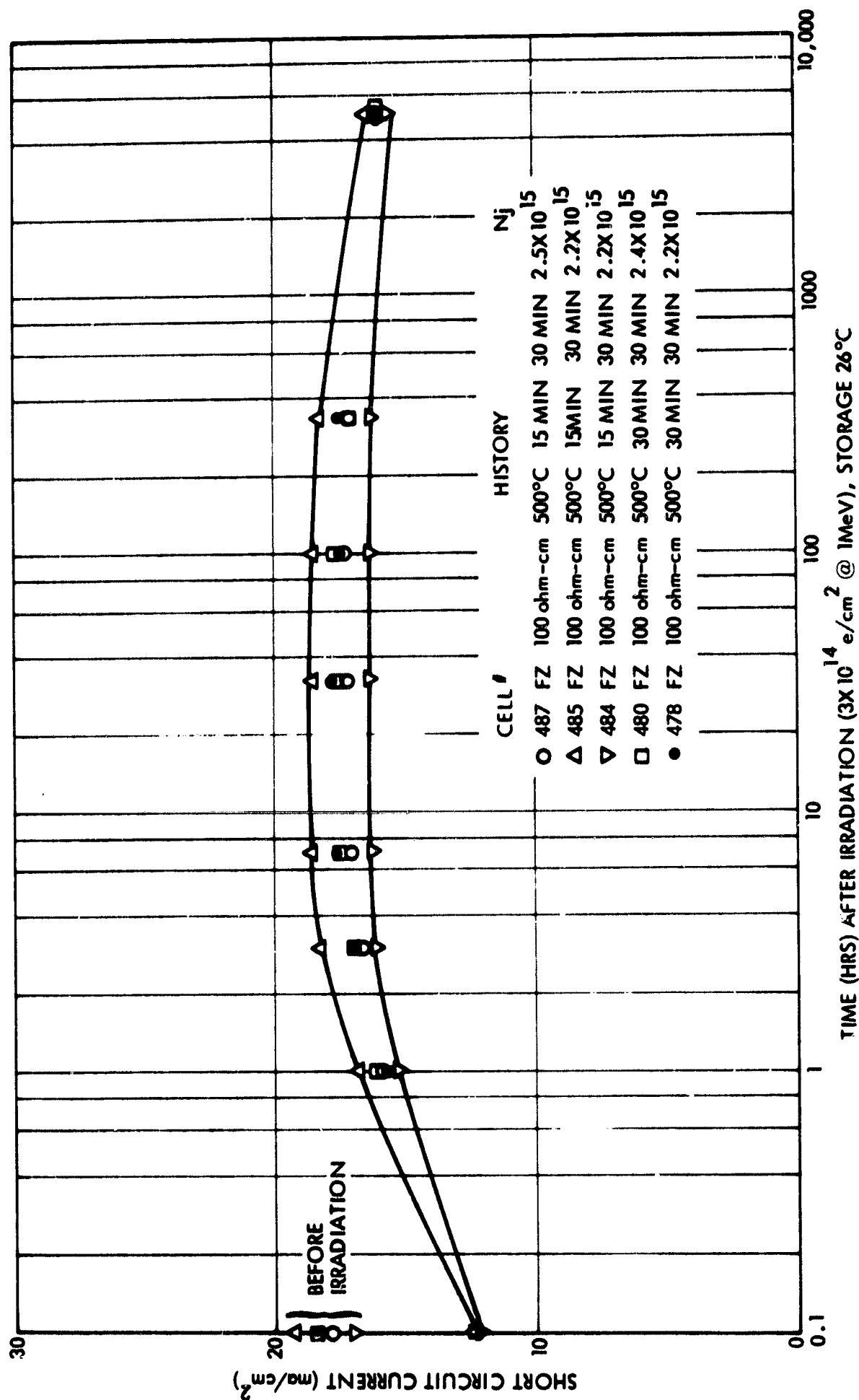


FIGURE 11. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
HELIOTEK LITHIUM SOLAR CELLS, 500°C DIFFUSION

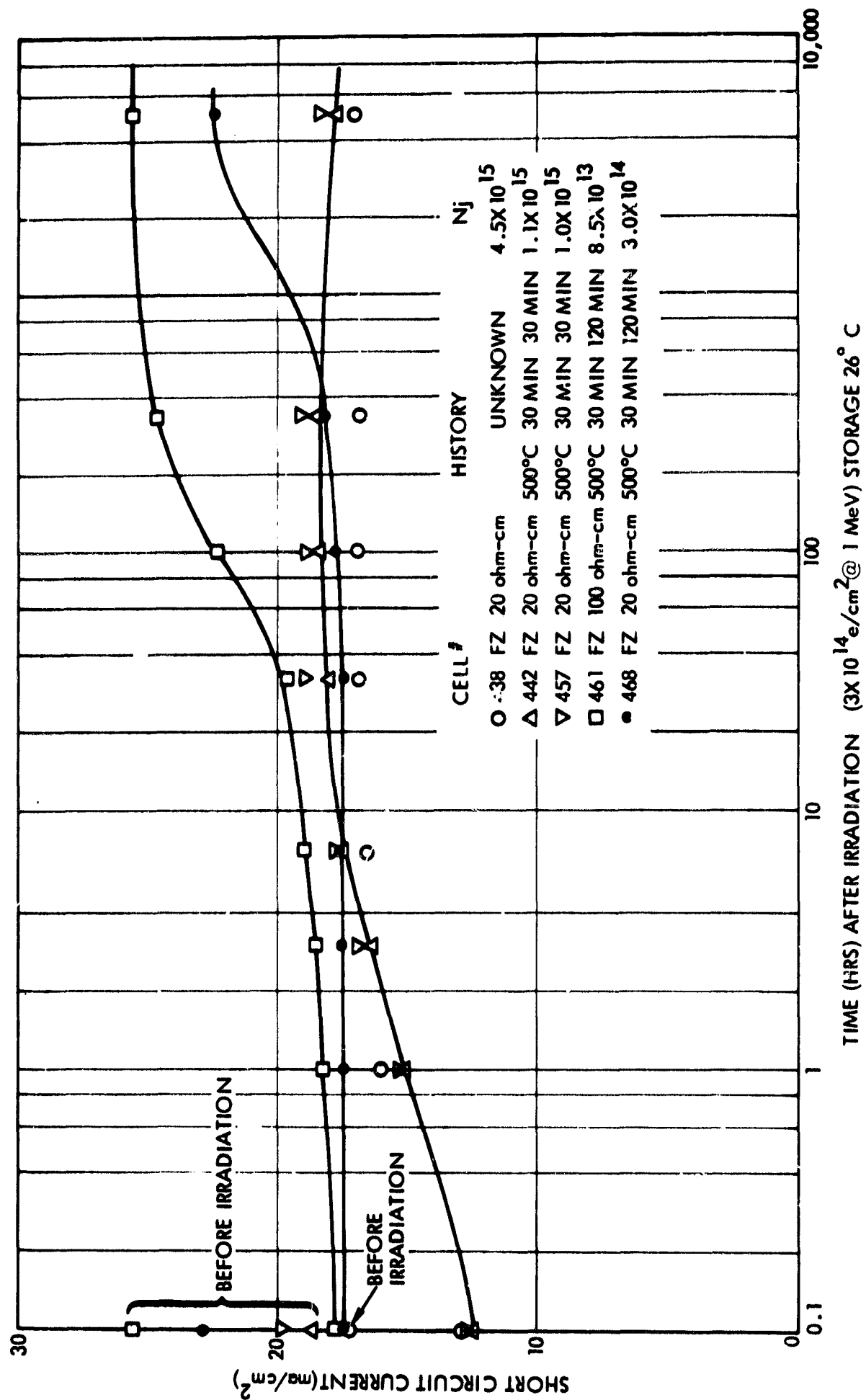


FIGURE 12. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
HELIOTEK LITHIUM SOLAR CELLS, 500°C DIFFUSION

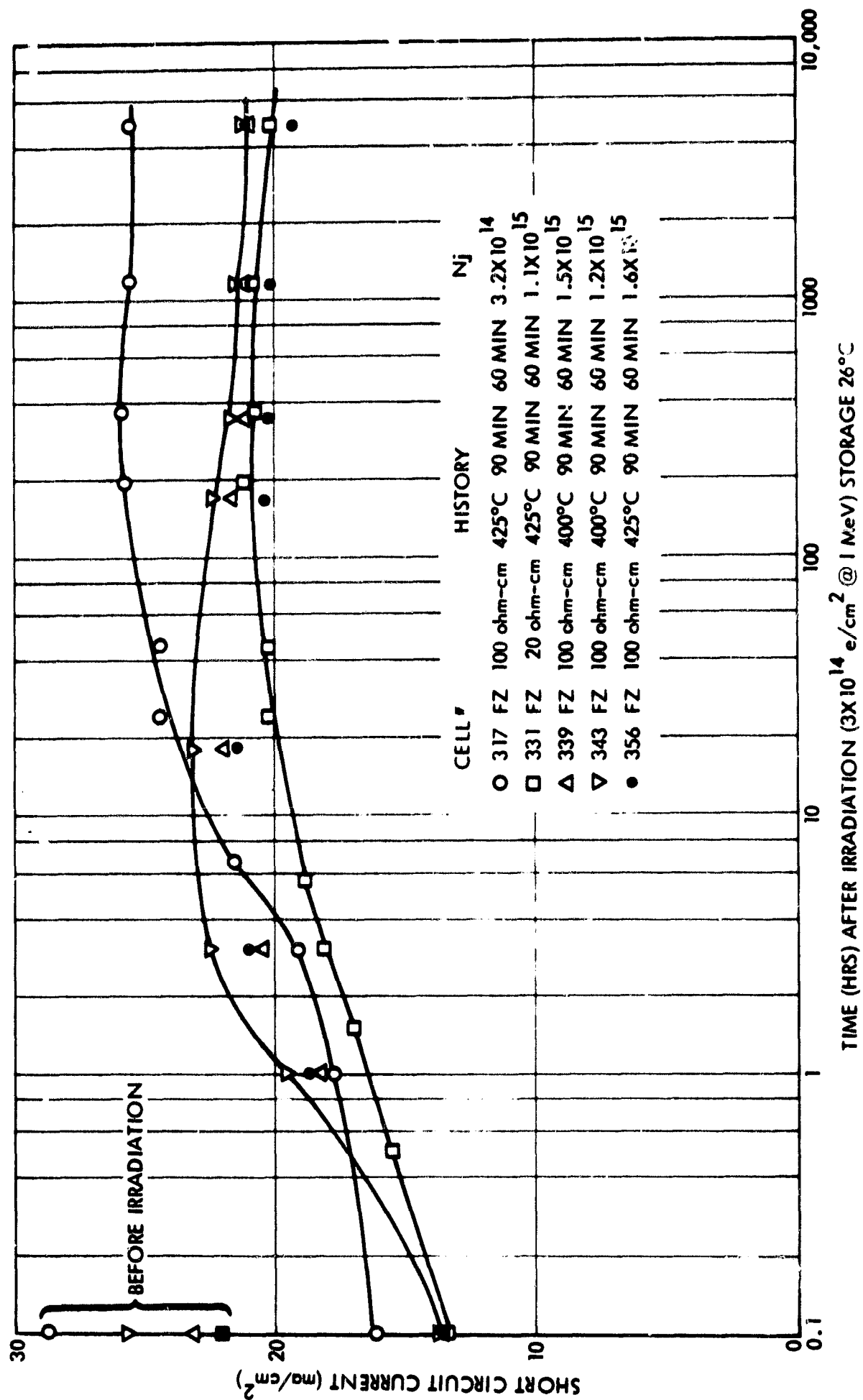


FIGURE 13. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
HELIOTEK LITHIUM SOLAR CELLS, 400-500°C DIFFUSION

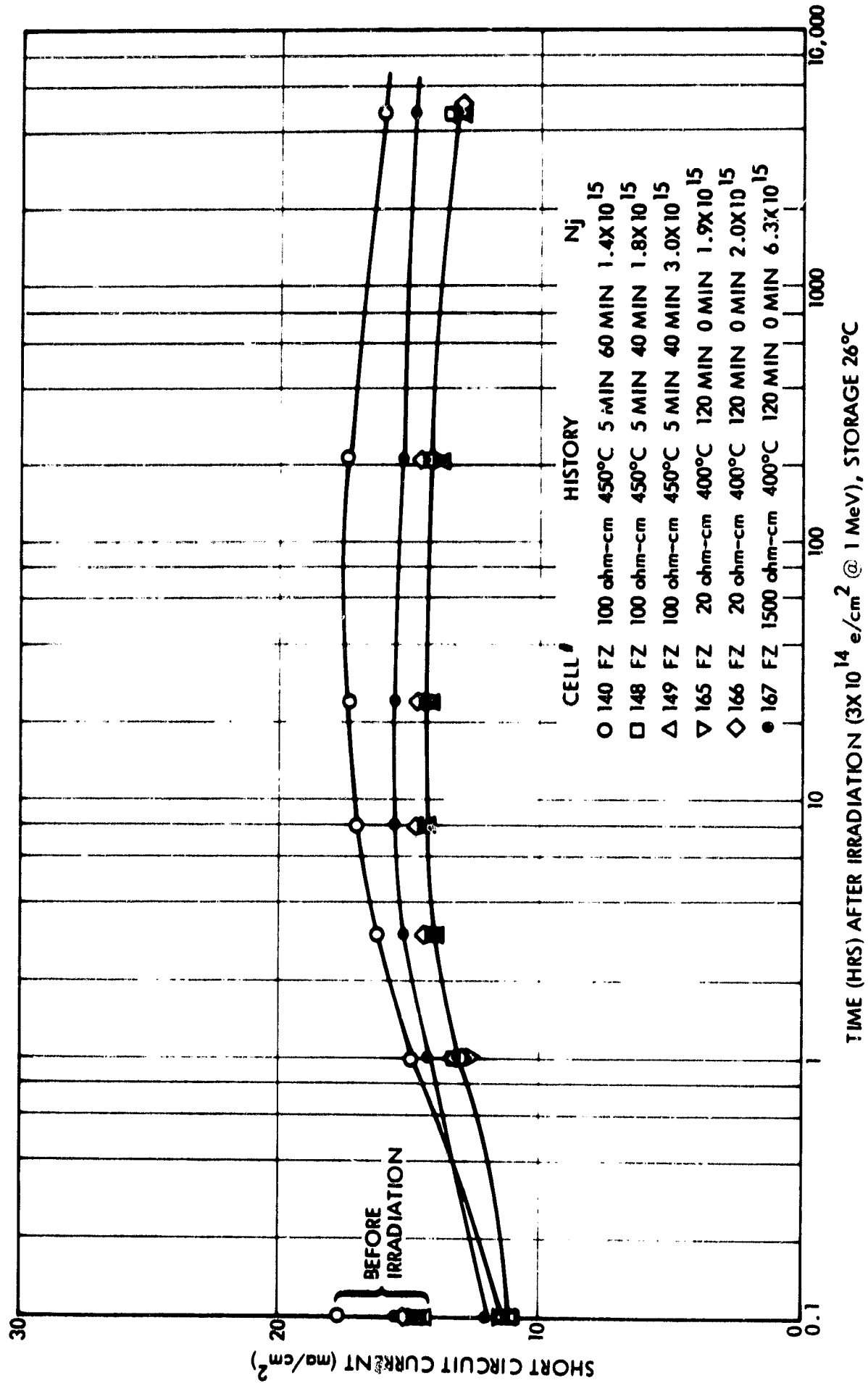


FIGURE 14. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
CENTRALAB LITHIUM SOLAR CELLS

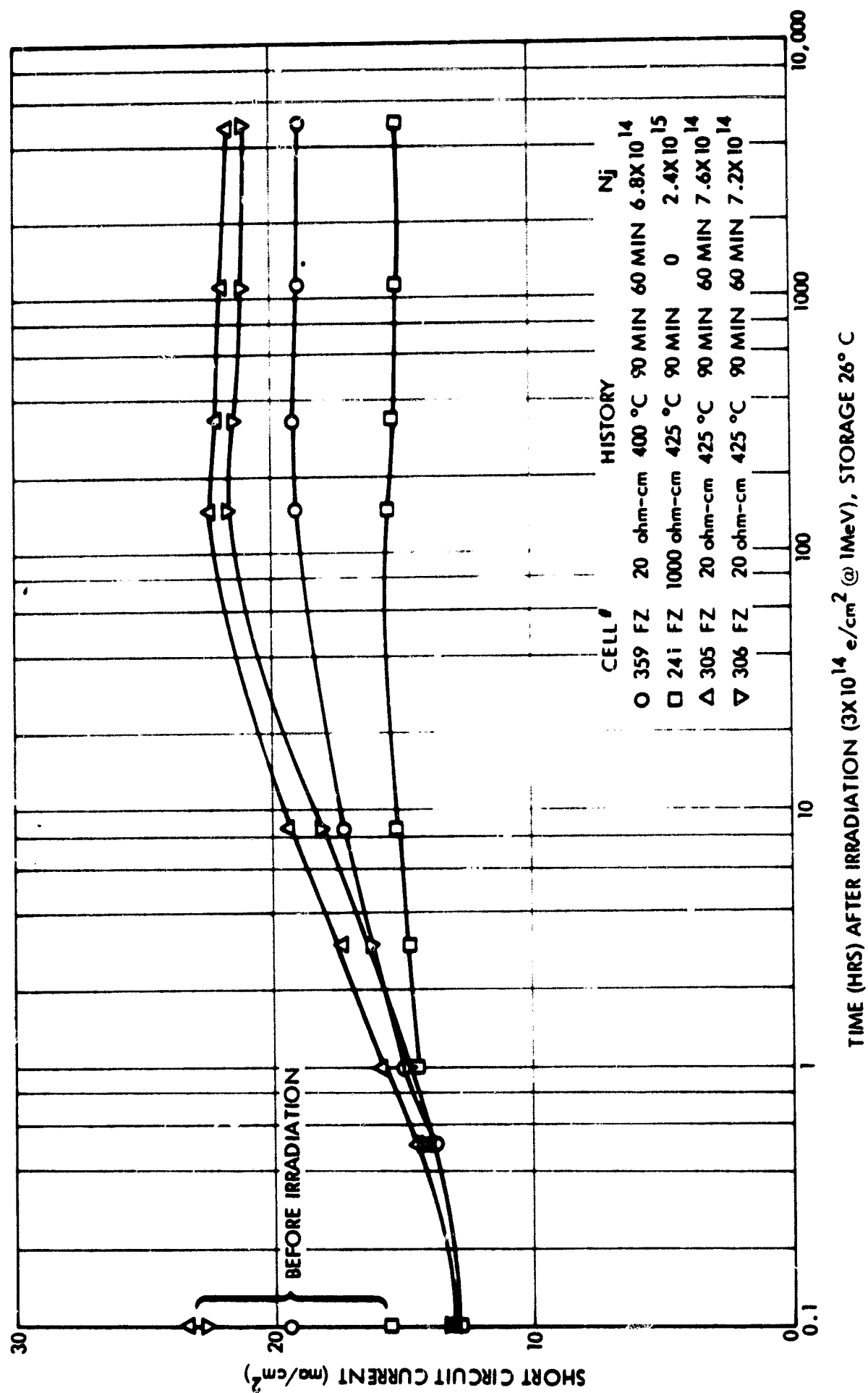


FIGURE 15. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
HELIOTEK LITHIUM SOLAR CELLS

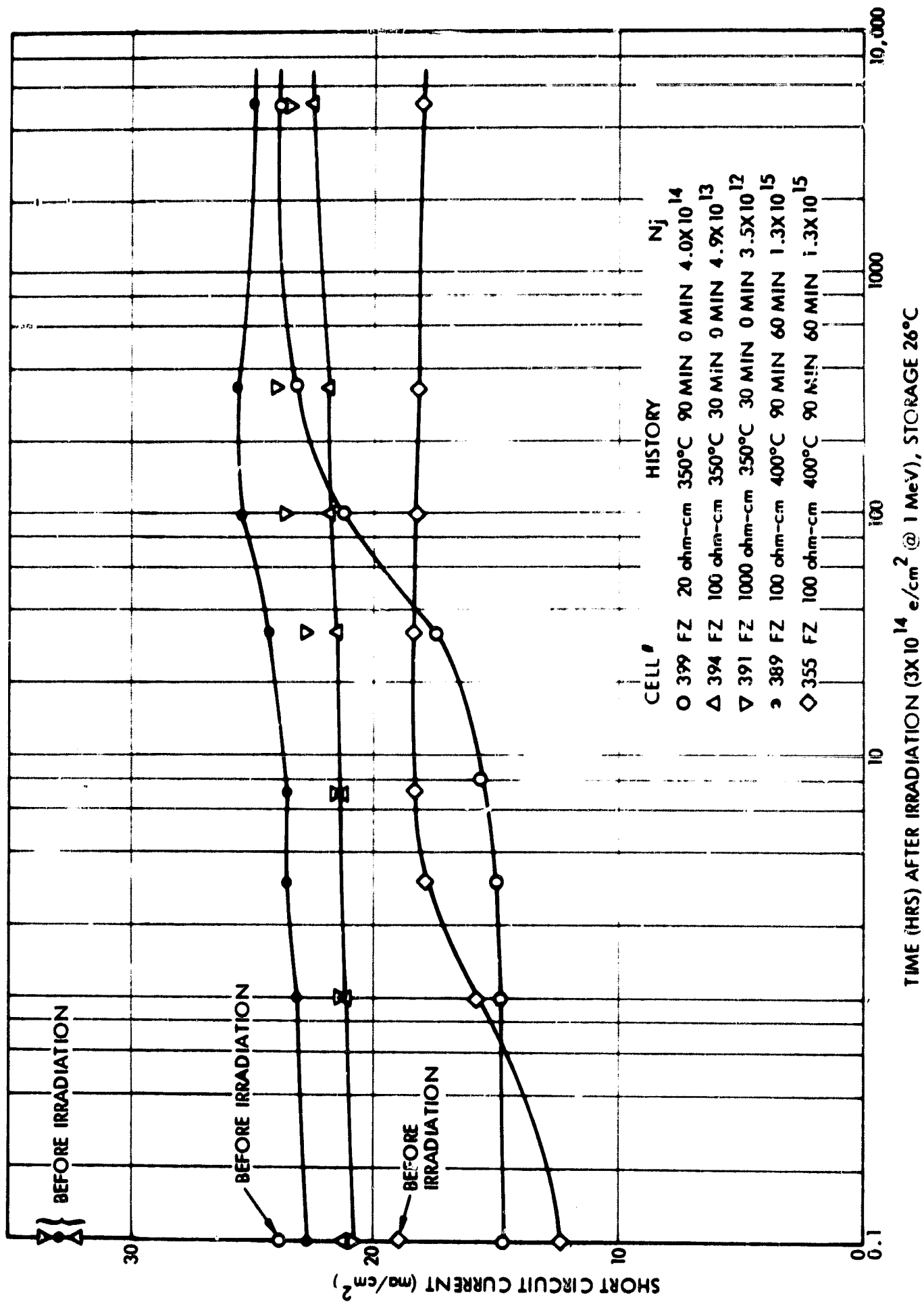


FIGURE 16. RECOVERY OF SHORT CIRCUIT CURRENT OF IRRADIATED
HELIOTEK LITHIUM SOLAR CELLS

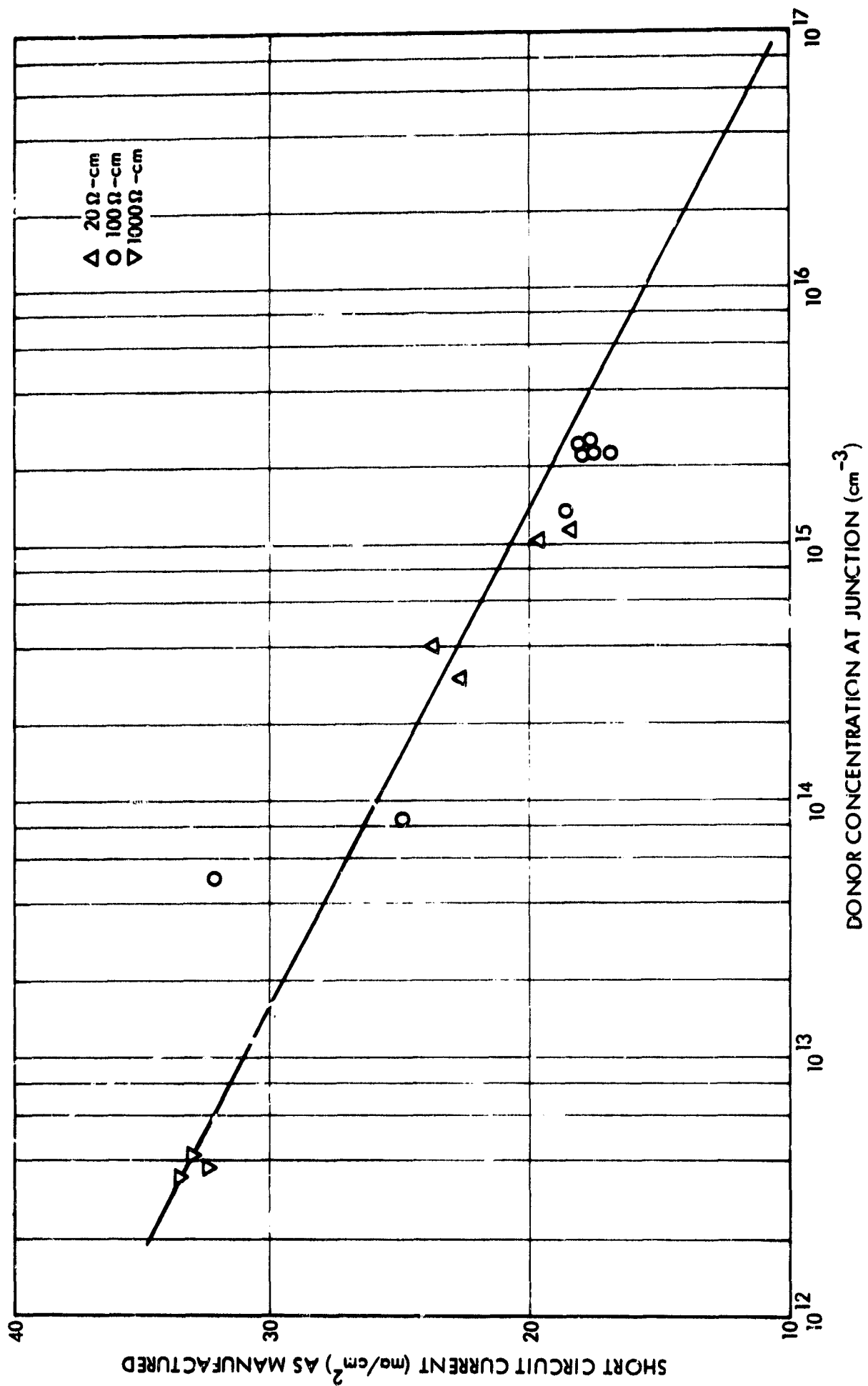


FIGURE 17. RELATIONSHIP OF LITHIUM CELL SHORT CIRCUIT CURRENT TO DONOR CONCENTRATION AT THE JUNCTION, HELIOTEK CELLS

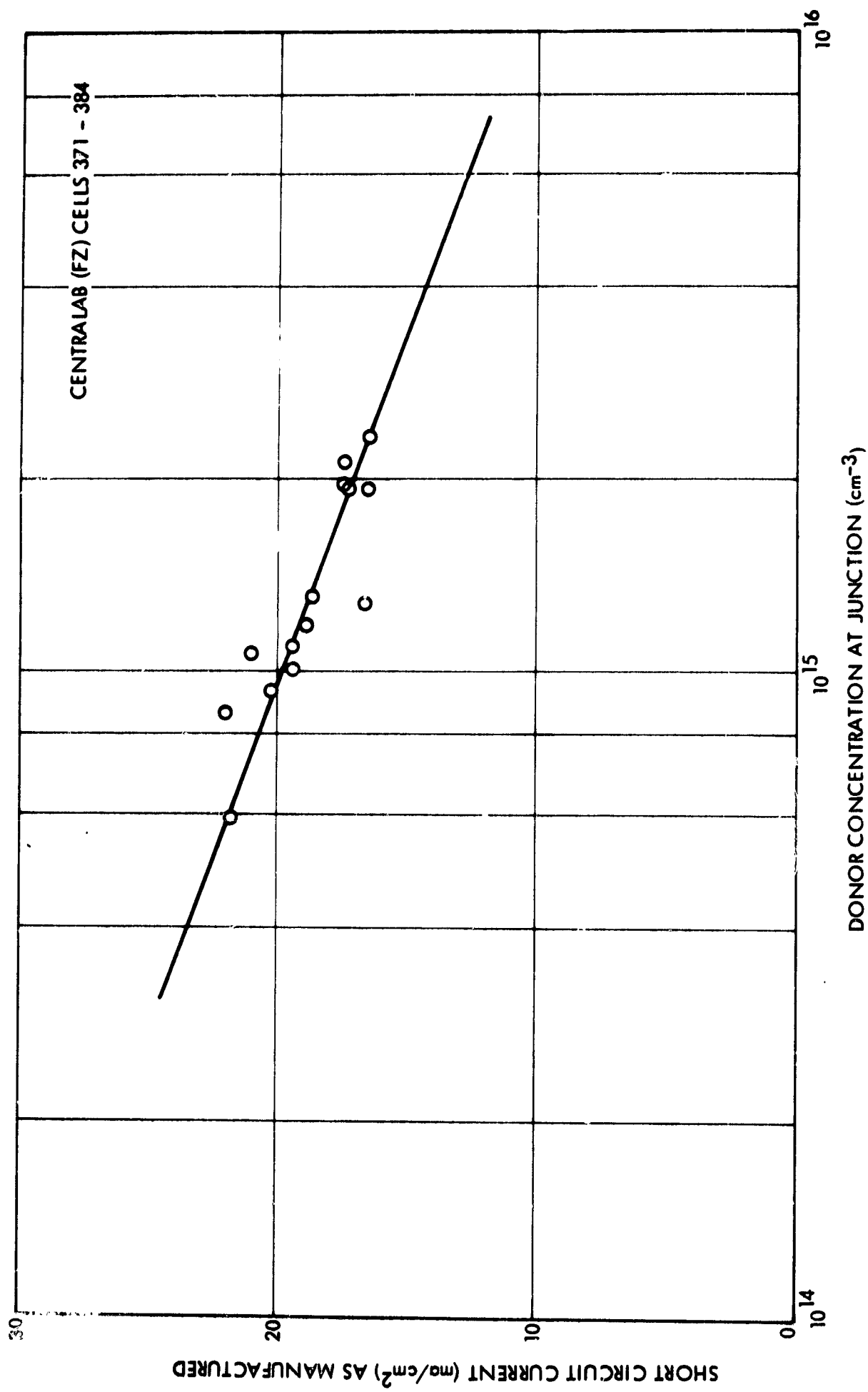


FIGURE 18. RELATIONSHIP OF LITHIUM CELL SHORT CIRCUIT CURRENT
TO DONOR CONCENTRATION AT THE JUNCTION, CENTRALAB CELL

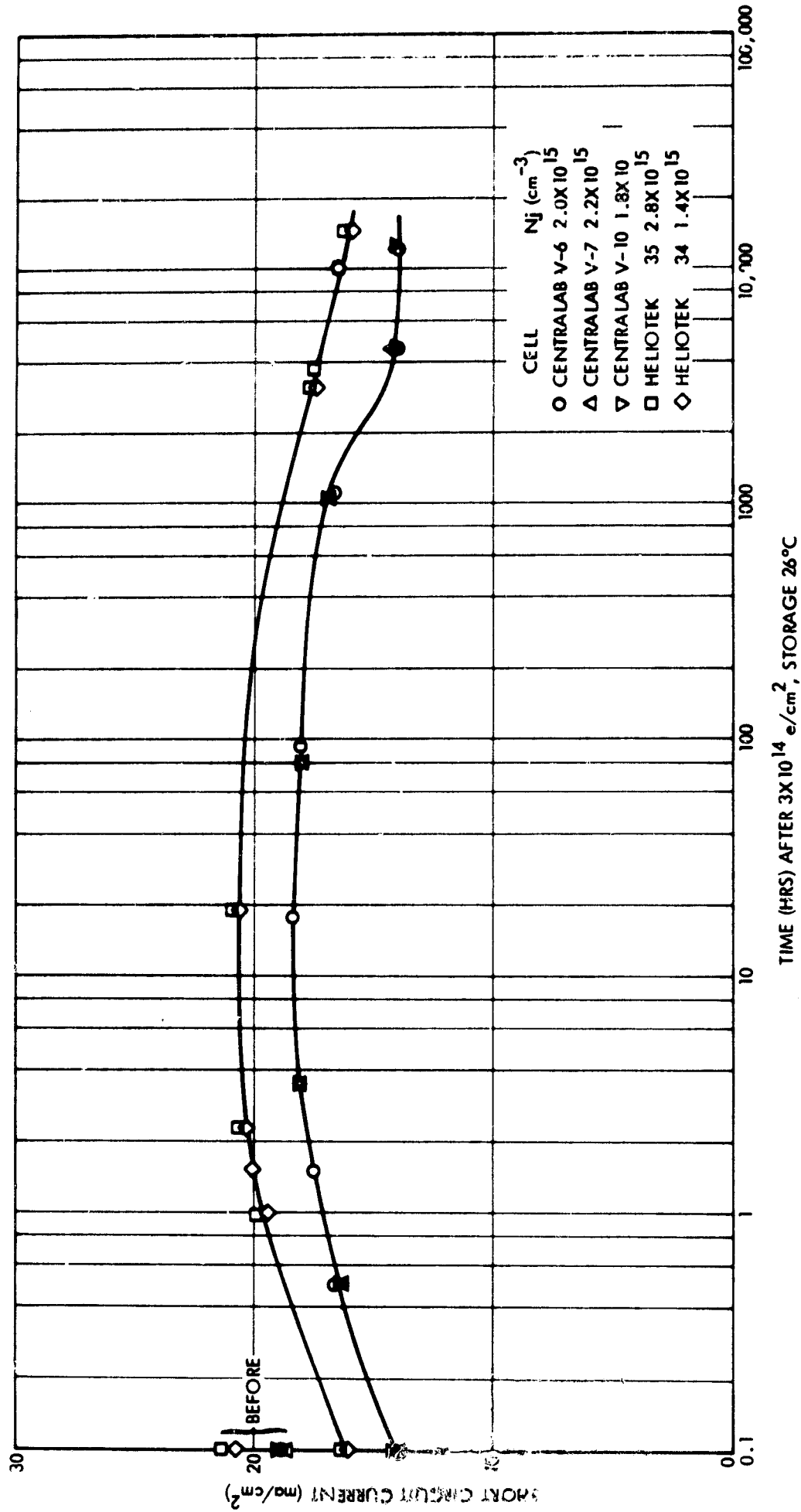


FIGURE 19. REDEGRADATION OF LITHIUM SOLAR CELLS

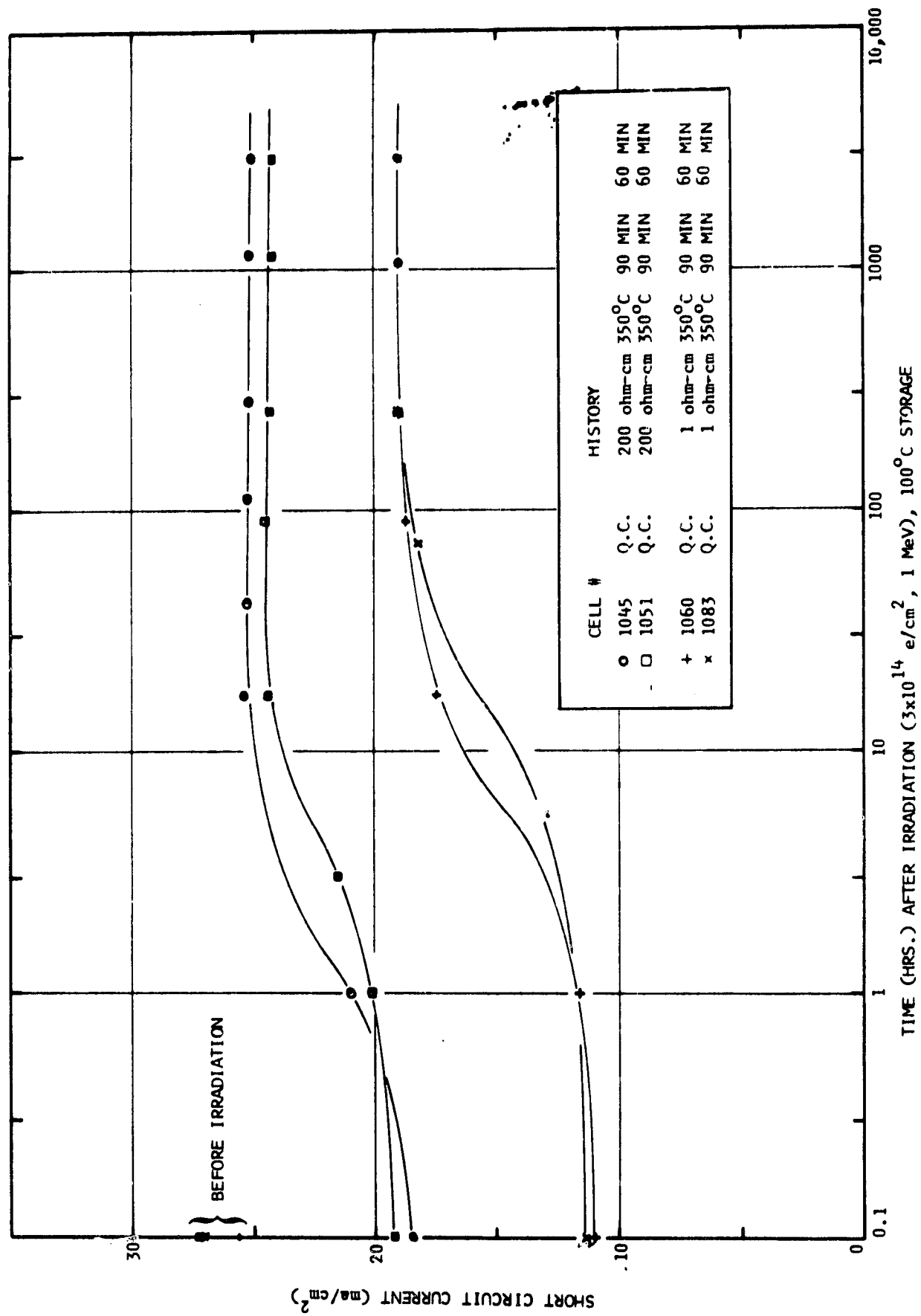


FIGURE 20. RECOVERY OF QUARTZ CRUCIBLE LITHIUM SOLAR CELLS

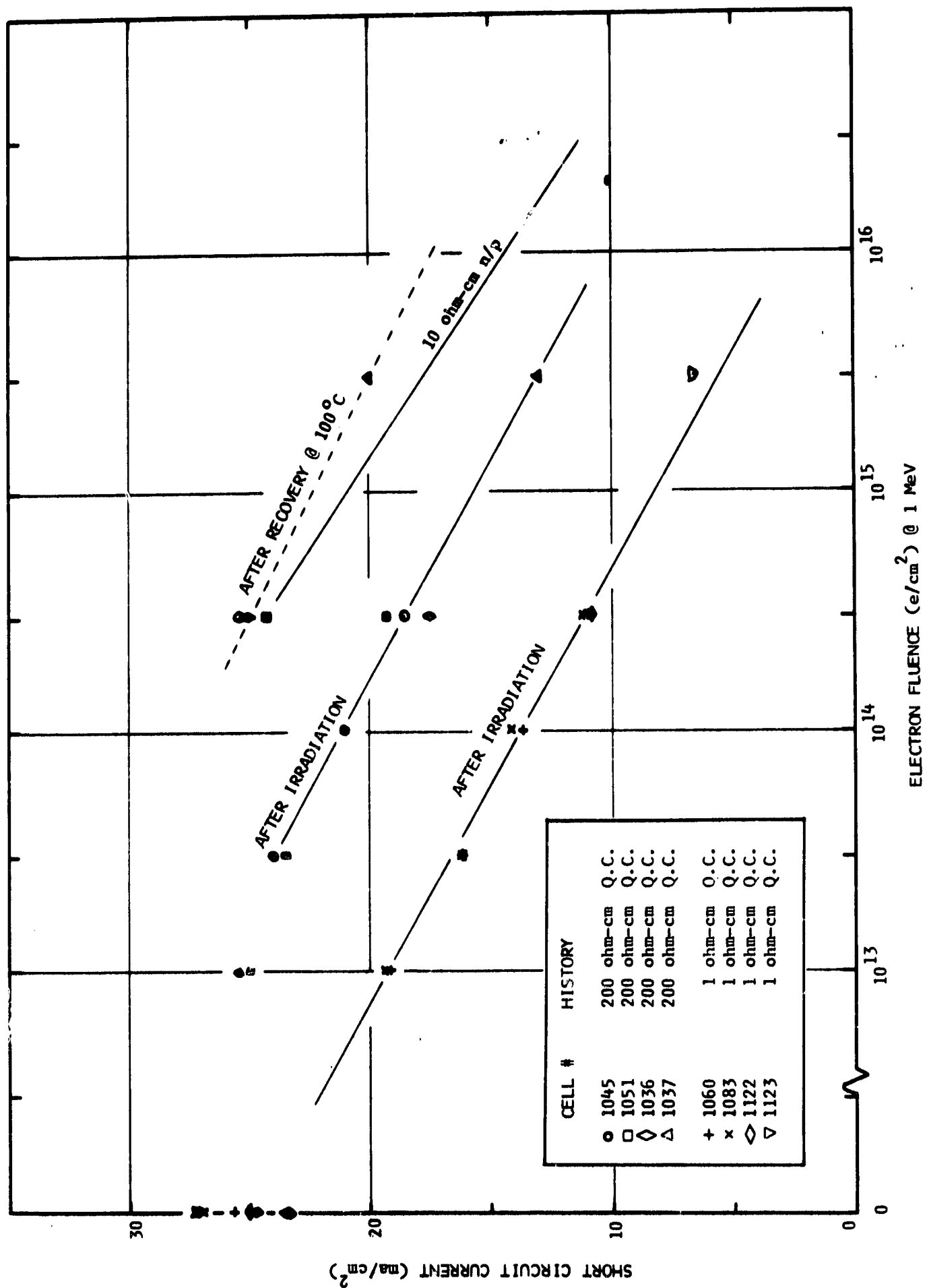


FIGURE 21. DEGRADATION AND RECOVERY OF QUARTZ CRUCIBLE
LITHIUM SOLAR CELLS

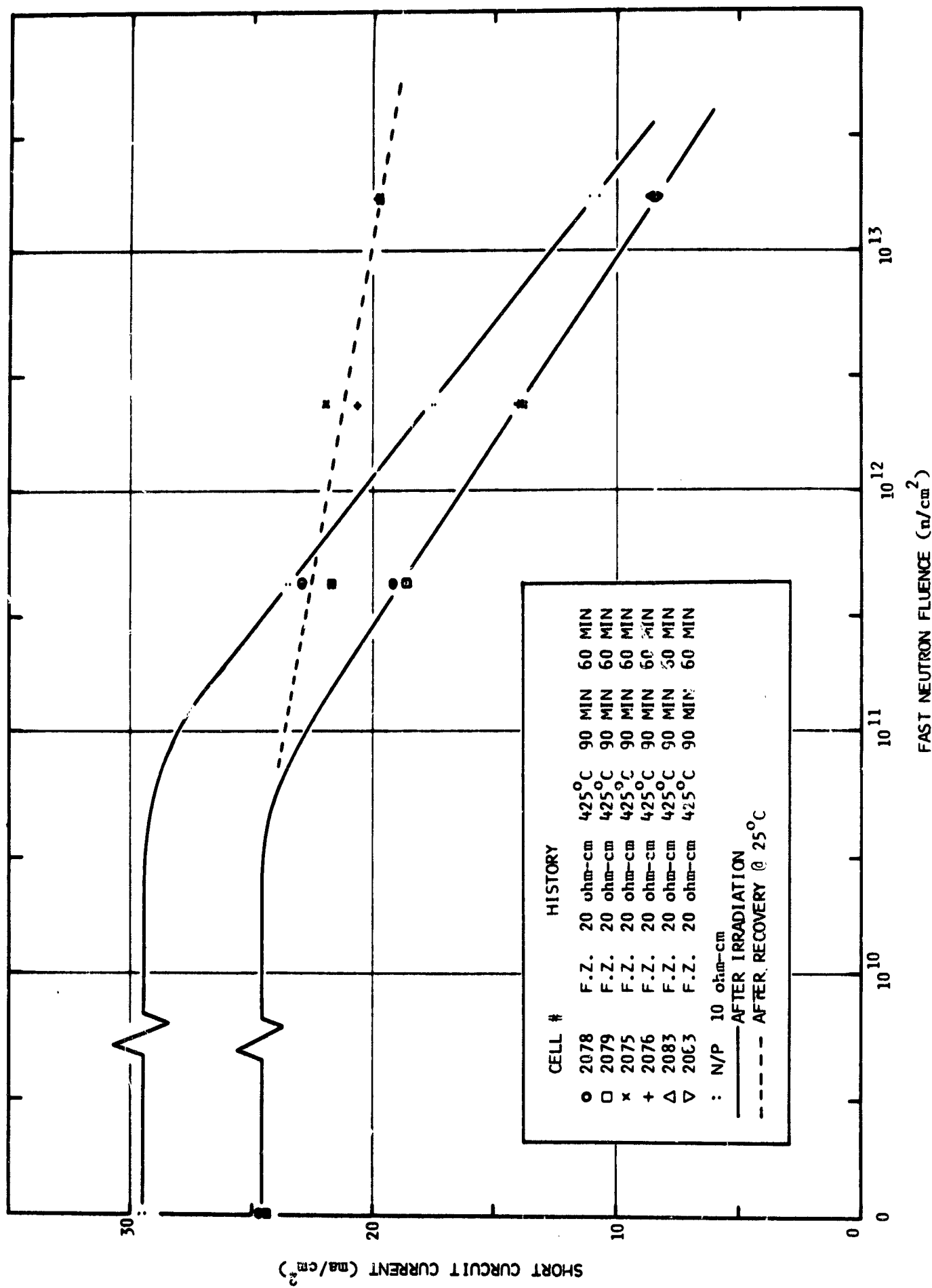


FIGURE 22. DEGRADATION AND RECOVERY OF LITHIUM SOLAR CELLS FROM FIRST NEUTRON IRRADIATION

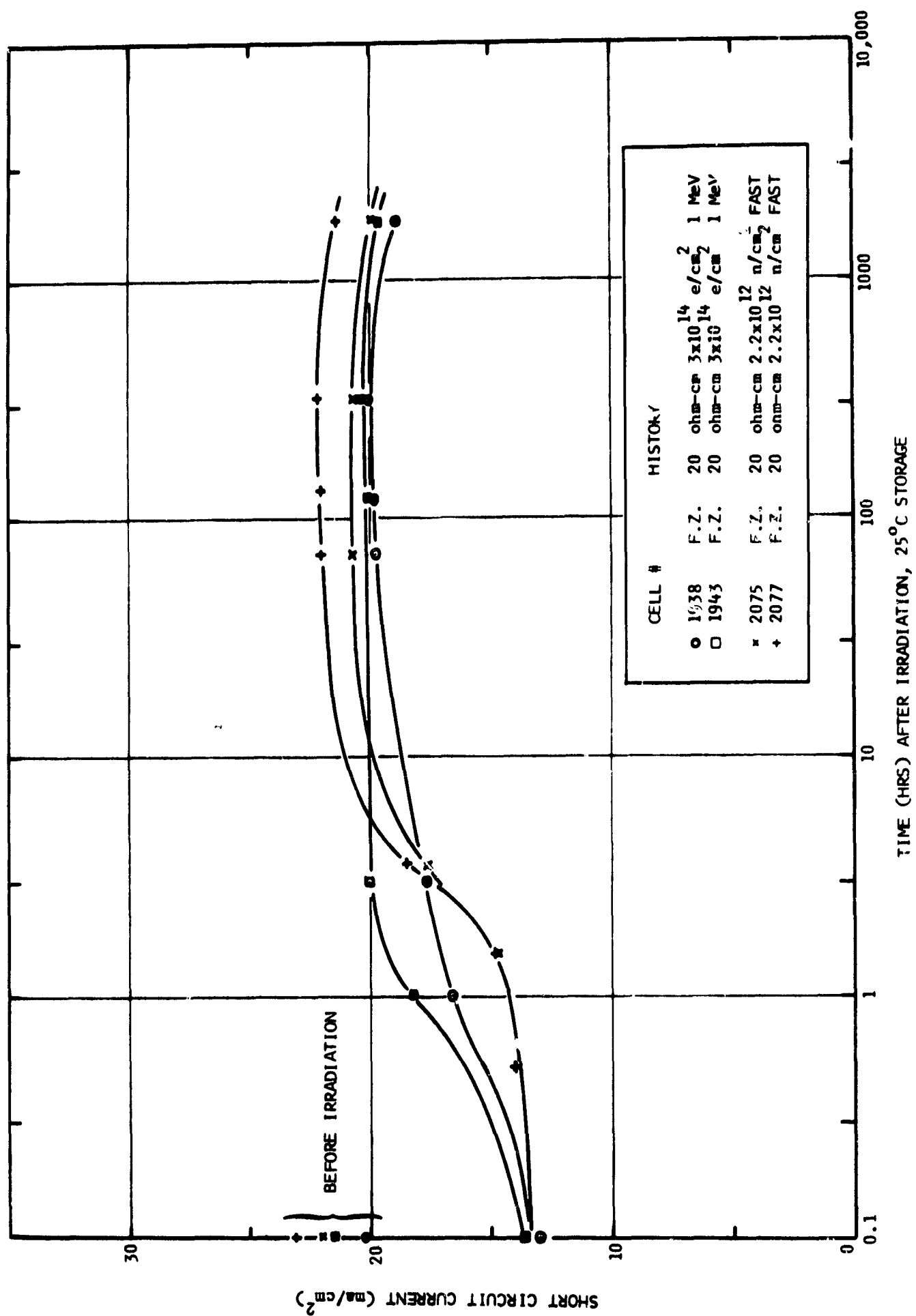


FIGURE 23. COMPARATIVE RECOVERY OF LITHIUM SOLAR CELLS
FROM NEUTRON AND ELECTRON IRRADIATION

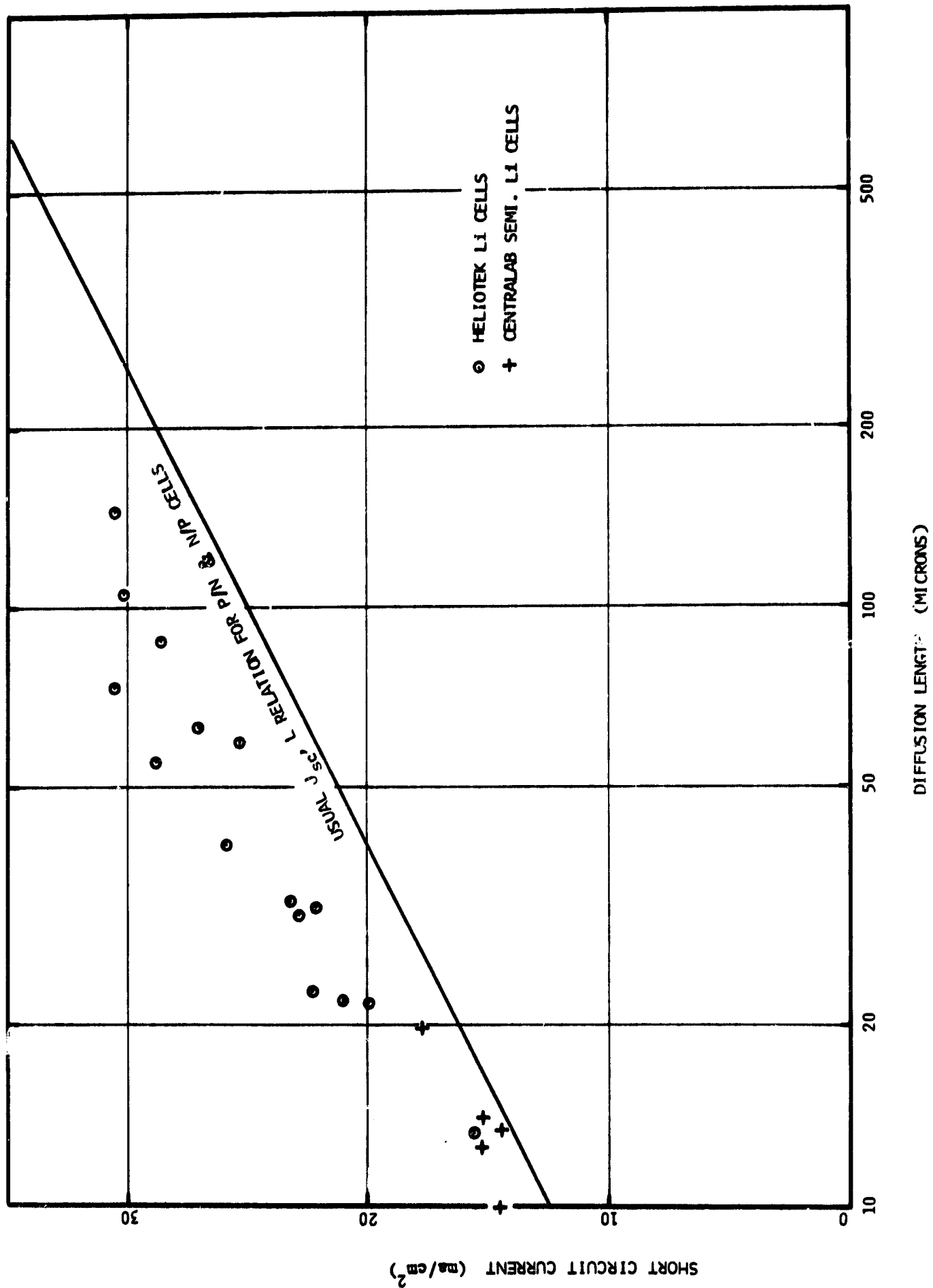


FIGURE 24. RELATIONSHIP OF SHORT CIRCUIT CURRENT AND DIFFUSION LENGTH FOR UNIRRADIATED LITHIUM SOLAR CELLS

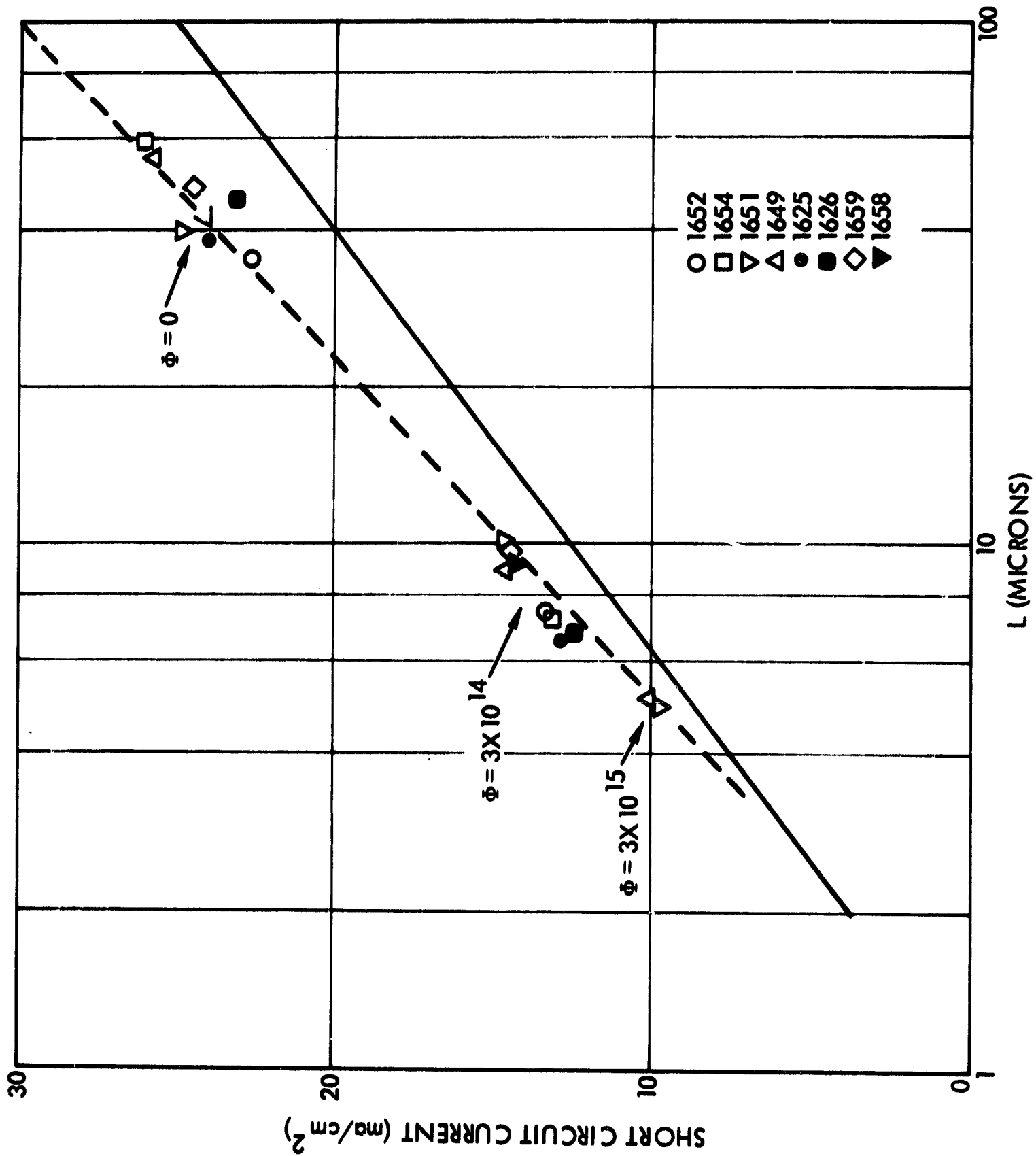


FIGURE 25. RELATIONSHIP OF SHORT CIRCUIT CURRENT AND DIFFUSION LENGTHS FOR ELECTRON IRRADIATED LITHIUM SOLAR CELLS

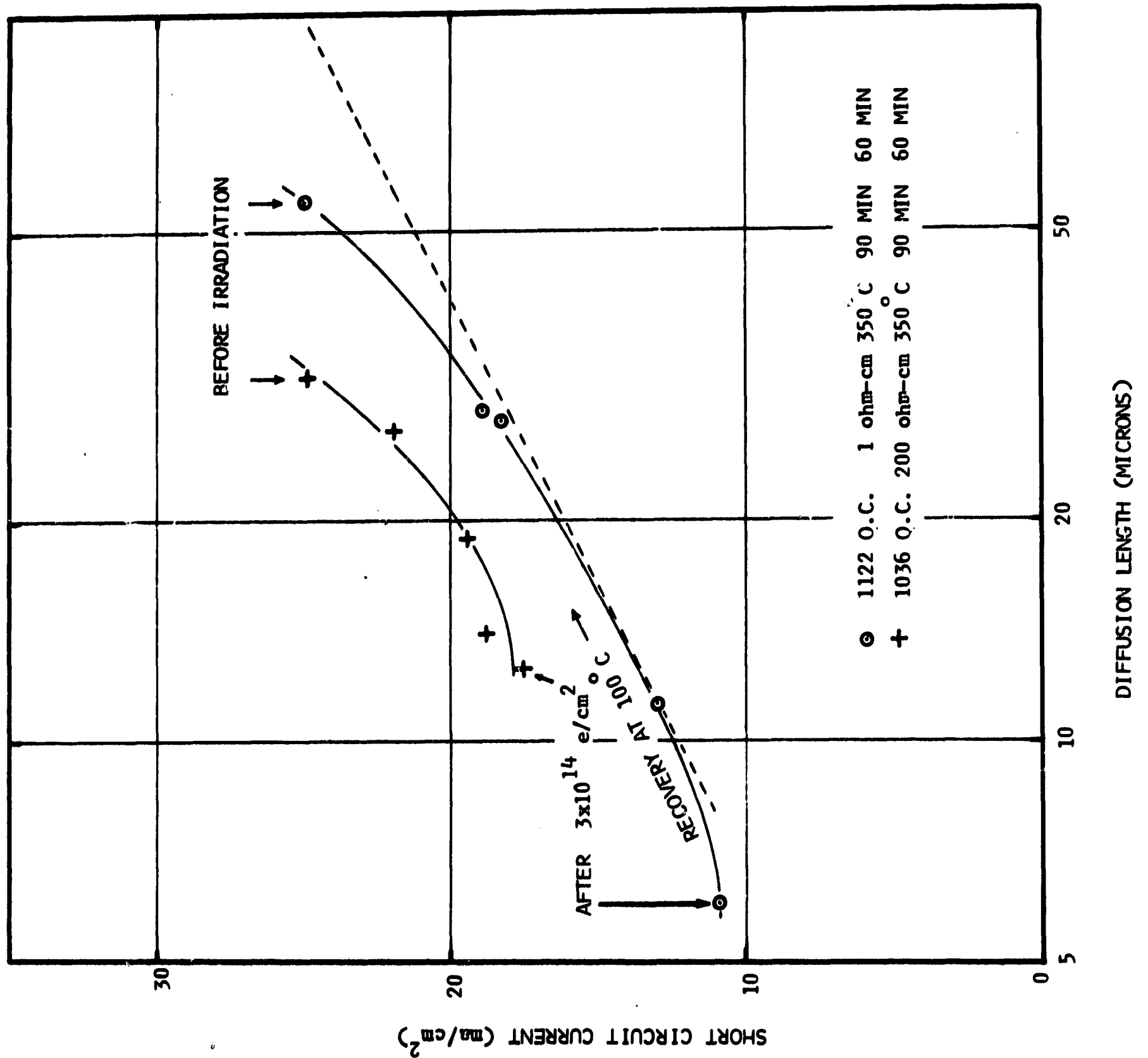


FIGURE 26. SHORT CIRCUIT CURRENT - DIFFUSION LENGTH CHANGES FOR IRRADIATION AND RECOVERY OF Q.C. LITHIUM SOLAR CELLS

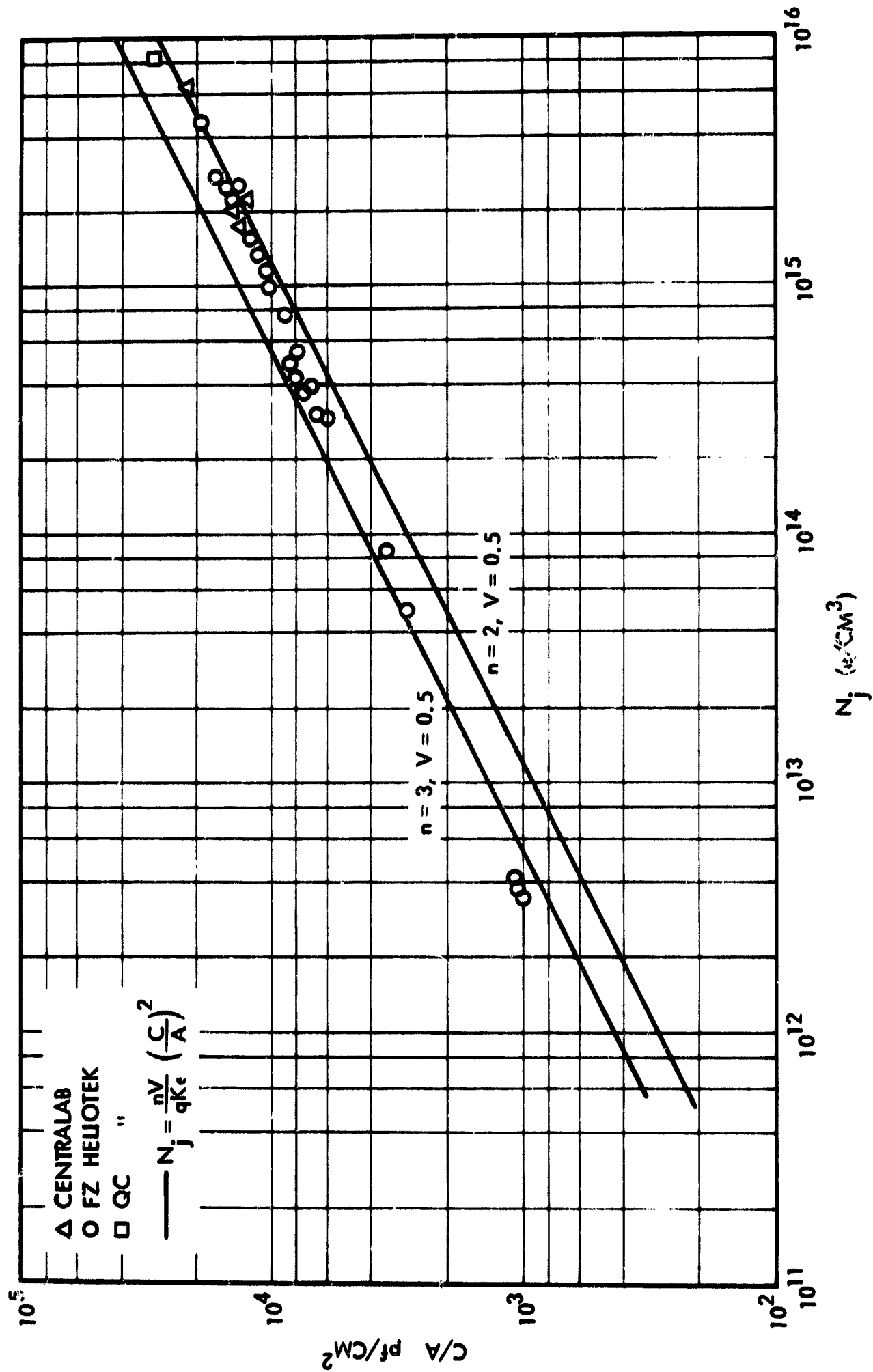


FIGURE 27. RELATIONSHIP OF JUNCTION CAPACITANCE AND DONOR CONCENTRATION

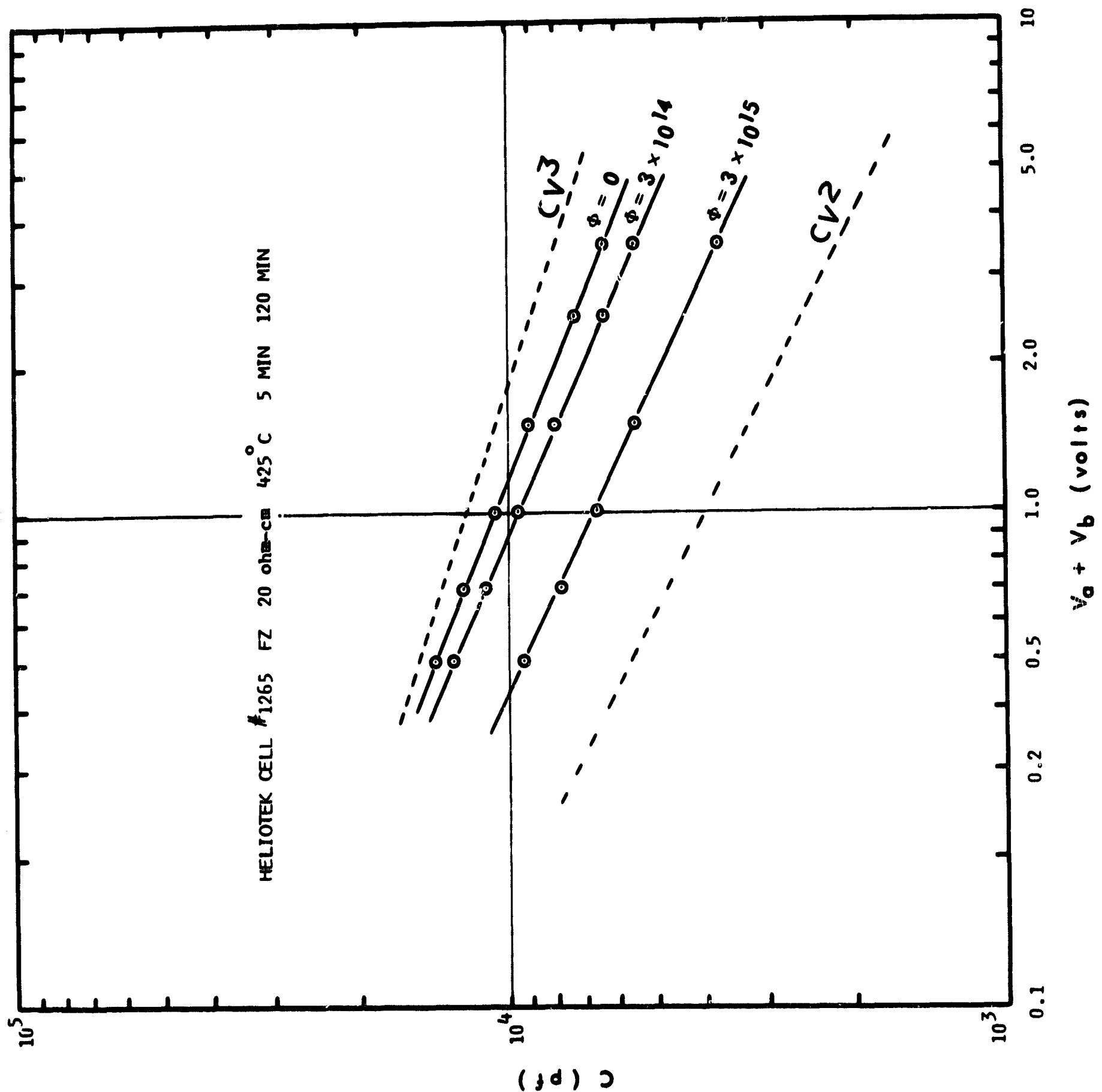


FIGURE 28. CAPACITANCE - VOLTAGE RELATIONS OF LITHIUM SOLAR CELL, VARIOUS ELECTRON IRRADIATIONS

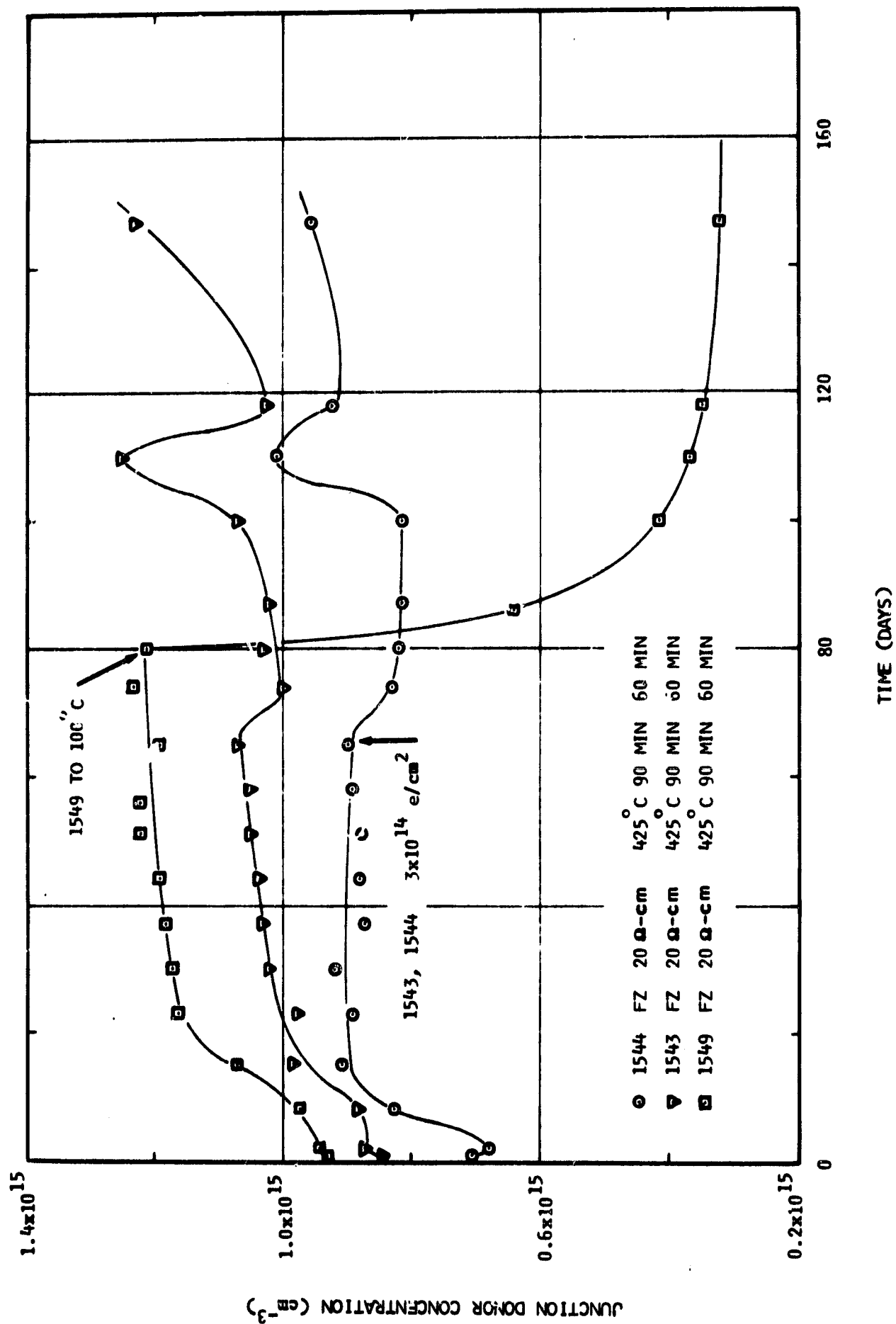


FIGURE 29. DONOR CONCENTRATION CHANGES AFTER MANUFACTURE OF
LITHIUM SOLAR CELLS

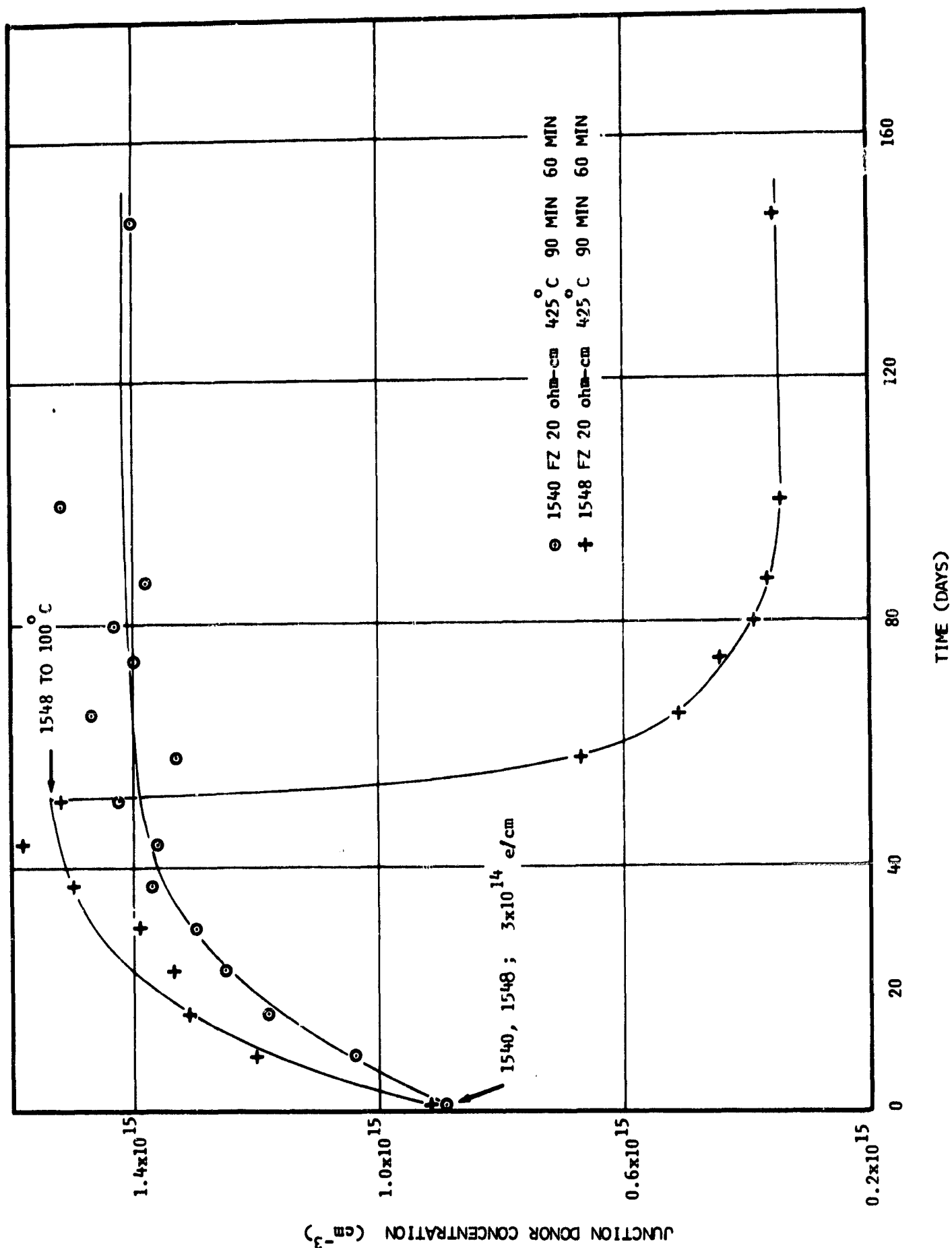


FIGURE 30. DONOR CONCENTRATION CHANGES AFTER MANUFACTURE OF LITHIUM SOLAR CELLS

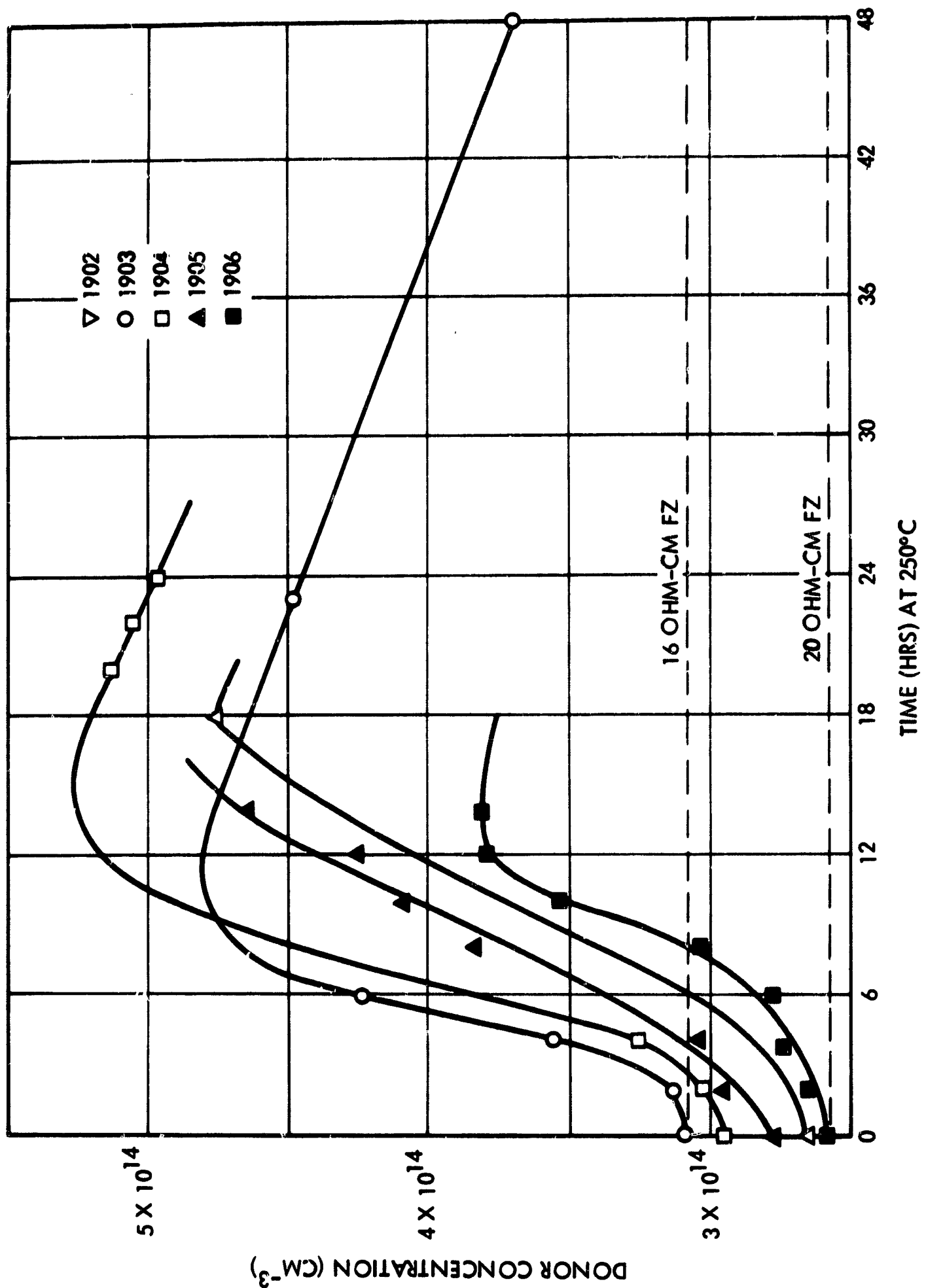


FIGURE 31. DONOR CONCENTRATION CHANGES DURING REDISTRIBUTION
OF LITHIUM SOLAR CELLS

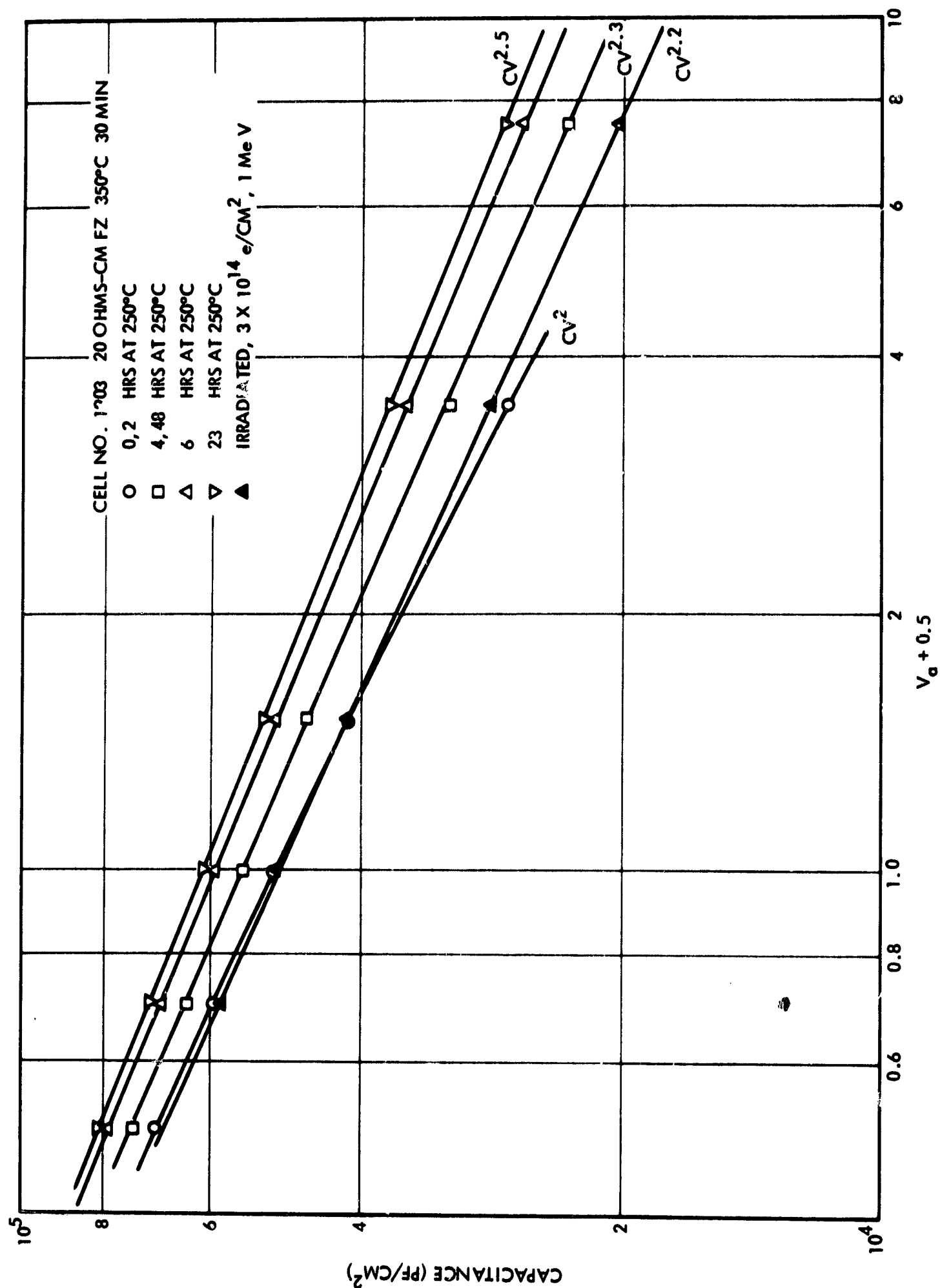


FIGURE 32. CAPACITANCE - VOLTAGE RELATIONS DURING REDISTRIBUTION OF LITHIUM SOLAR CELLS

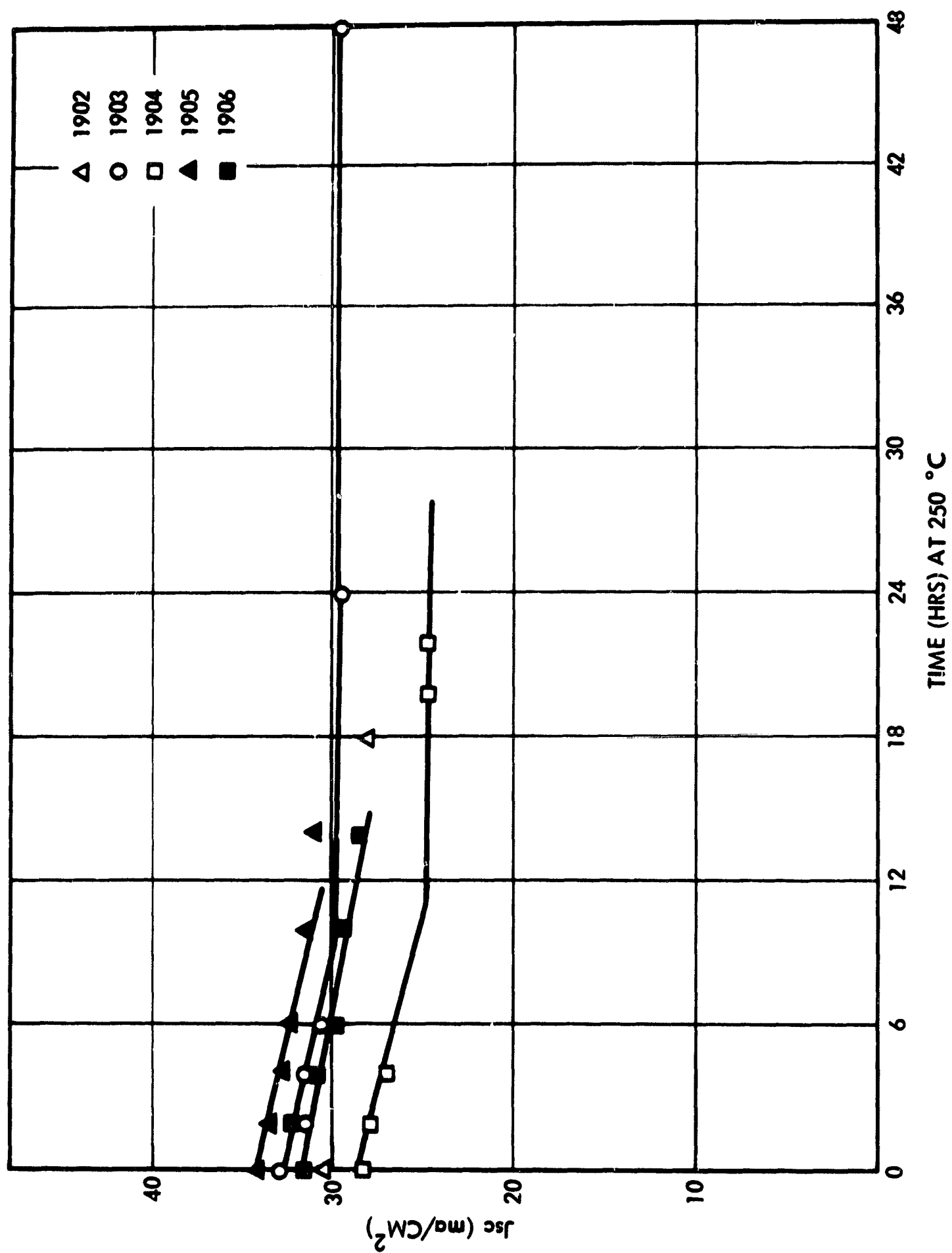


FIGURE 33. SHORT CIRCUIT CURRENT CHANGES DURING REDISTRIBUTION OF LITHIUM SOLAR CELLS

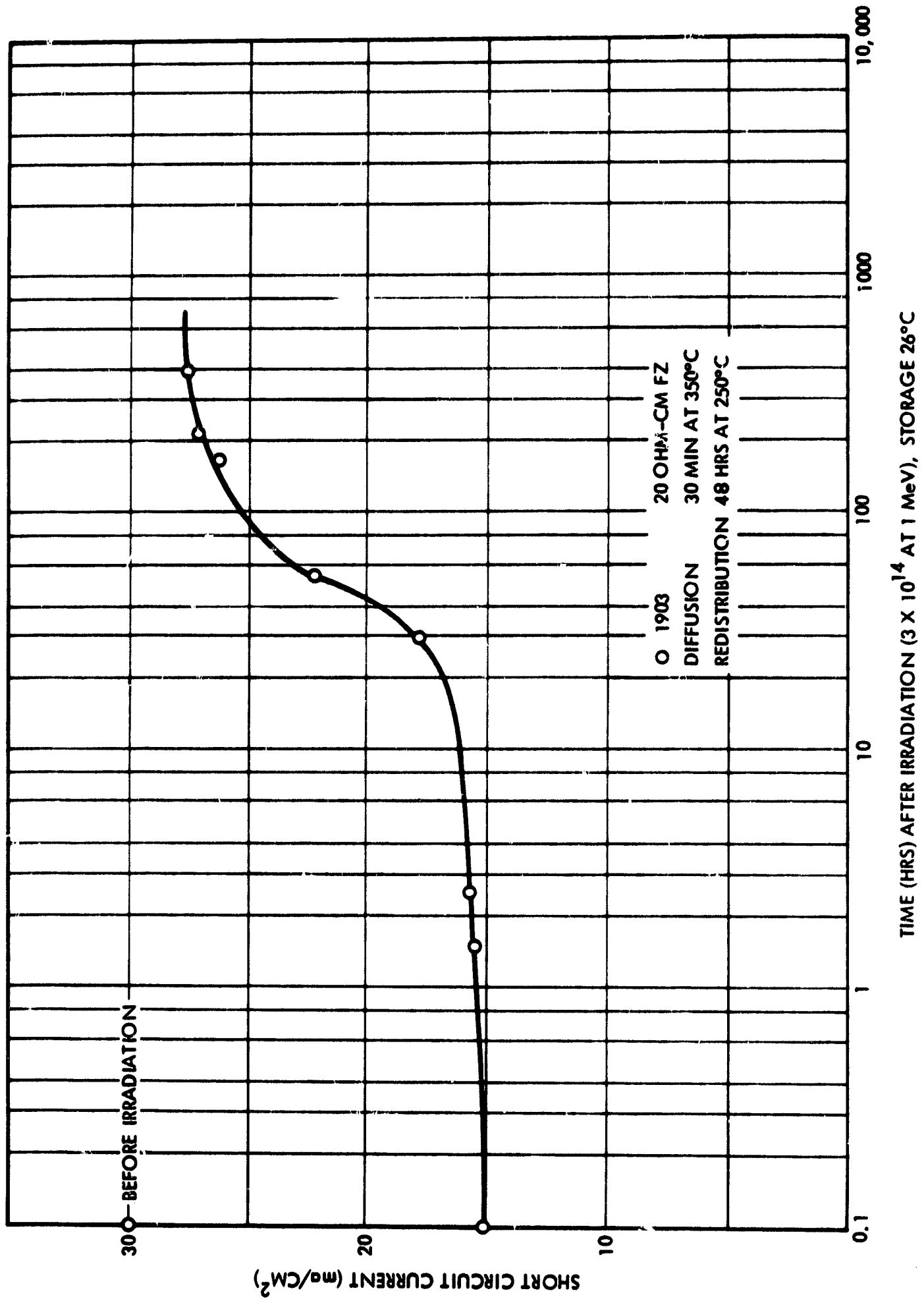


FIGURE 34. RECOVERY OF IRRADIATION OF LITHIUM SOLAR CELLS
WITH LOW TEMPERATURE REDISTRIBUTION

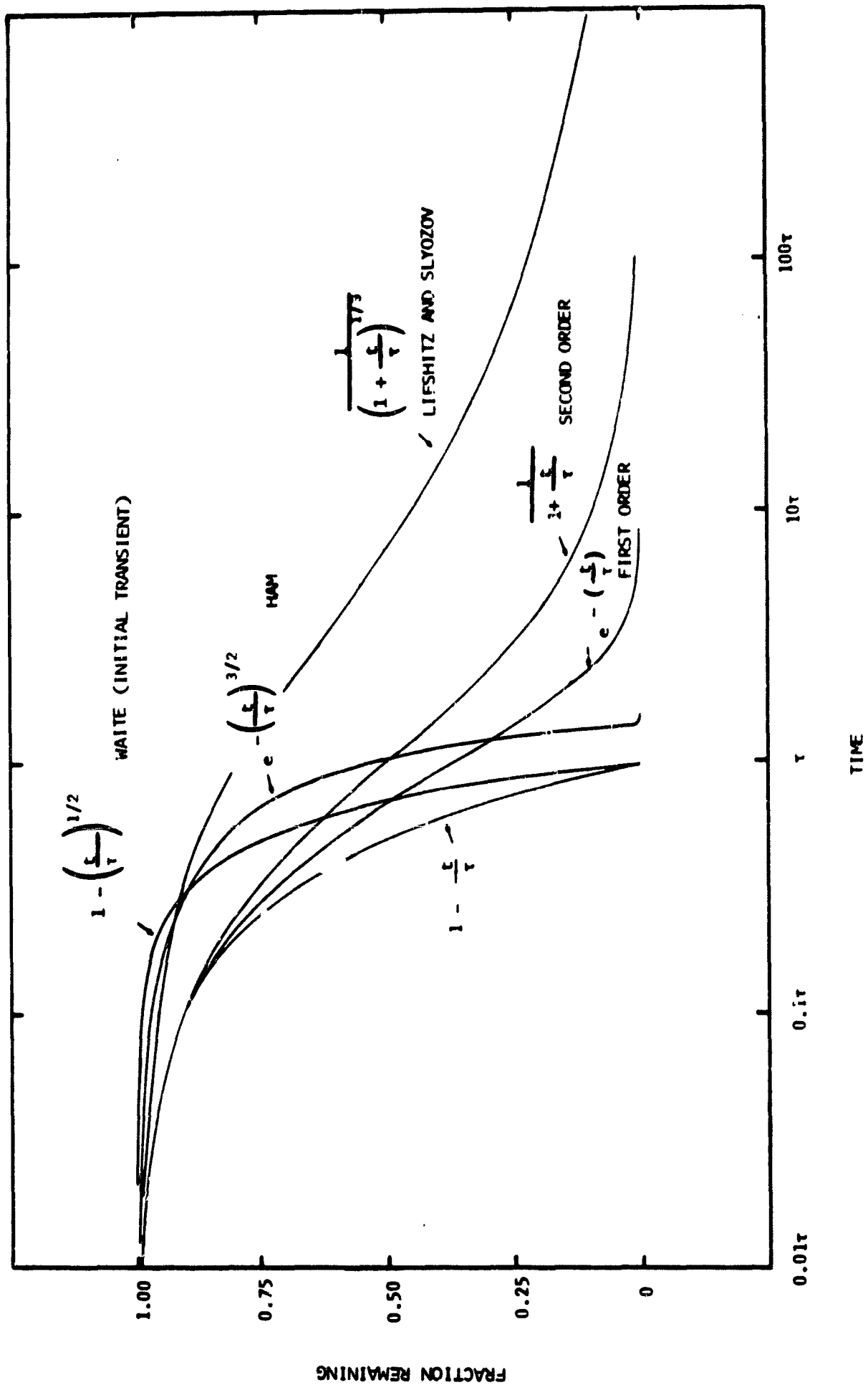


FIGURE 35. COMPARISON OF VARIOUS SOLID STATE REACTION KINETICS EQUATIONS

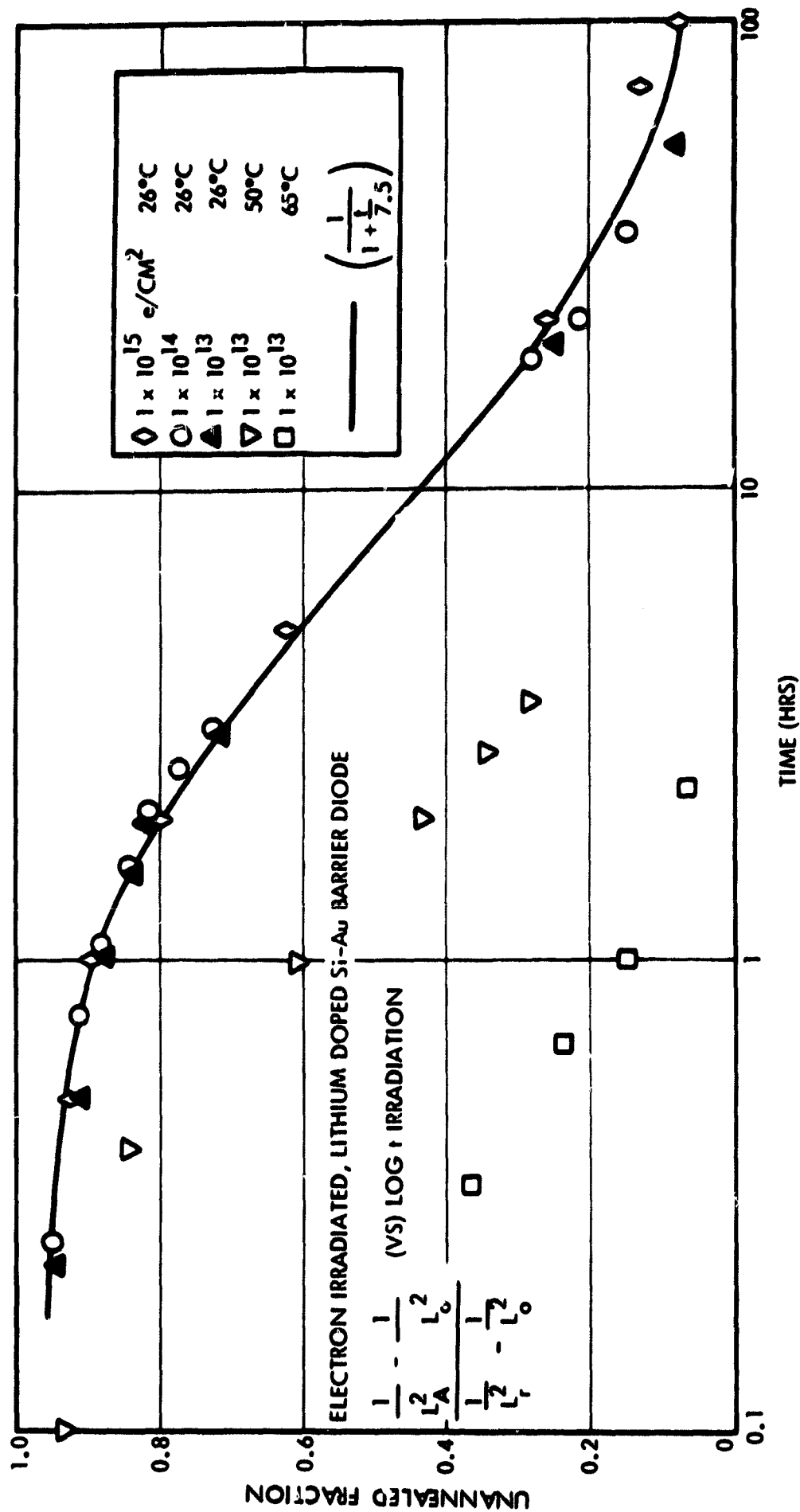


FIGURE 36. RECOVERY OF IRRADIATED LITHIUM DOPED
F.Z. Si-Au BARRIER DIODES

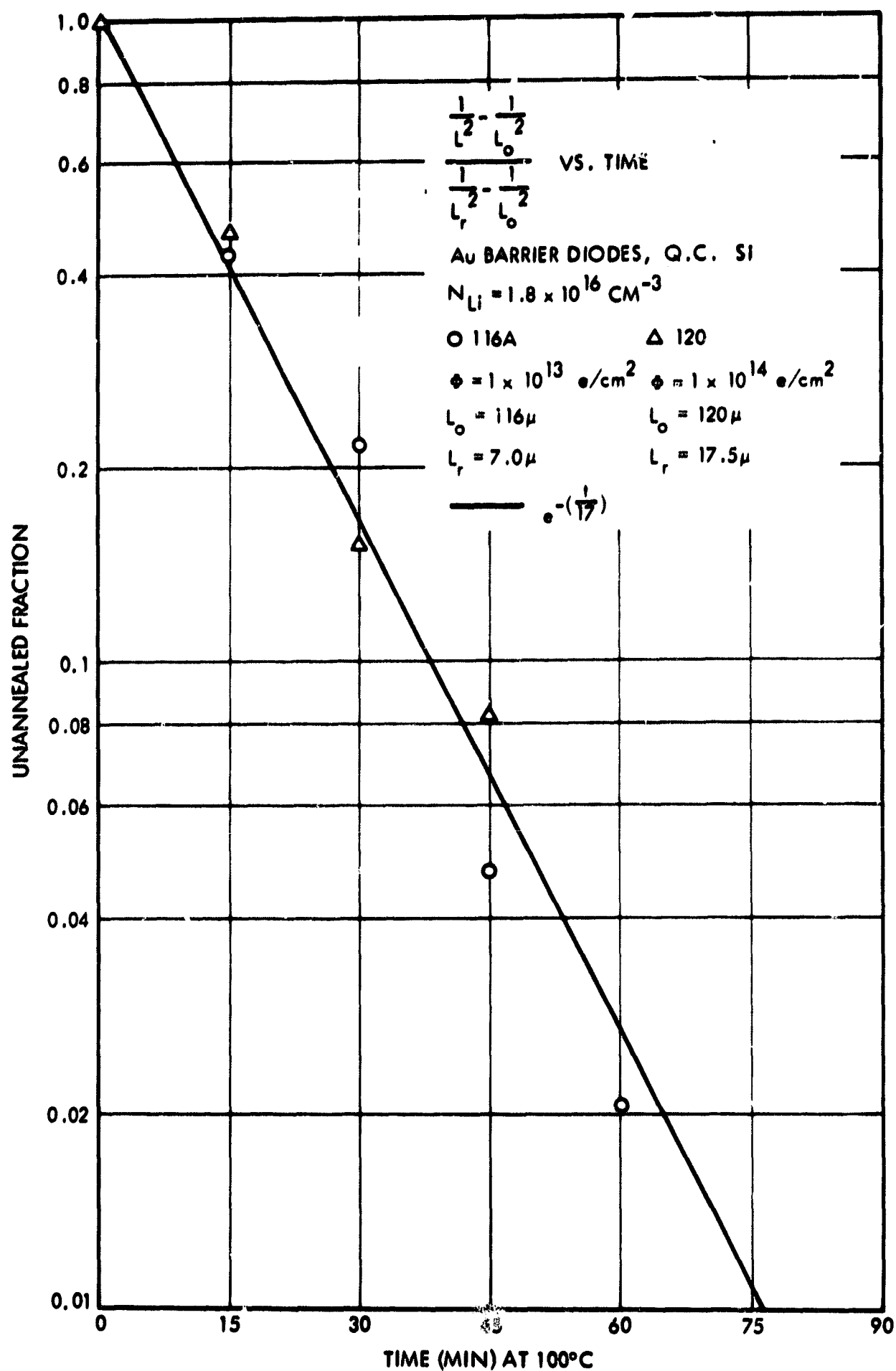


FIGURE 37. RECOVERY OF IRRADIATED LITHIUM DOPED
Q.C. Si-Au BARRIER DIODES

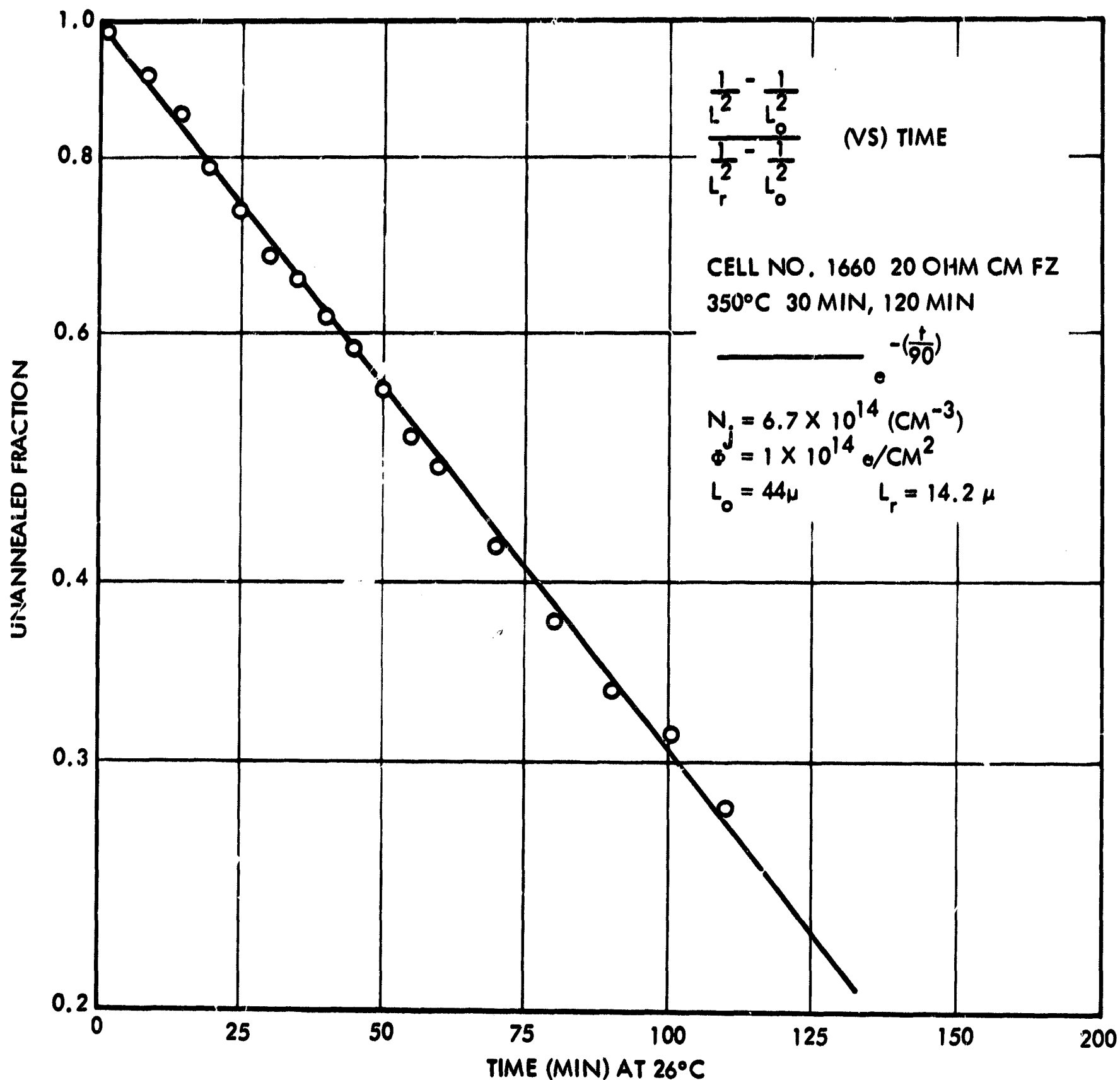


FIGURE 38. RECOVERY OF KINETICS OF IRRADIATED LITHIUM SOLAR CELL

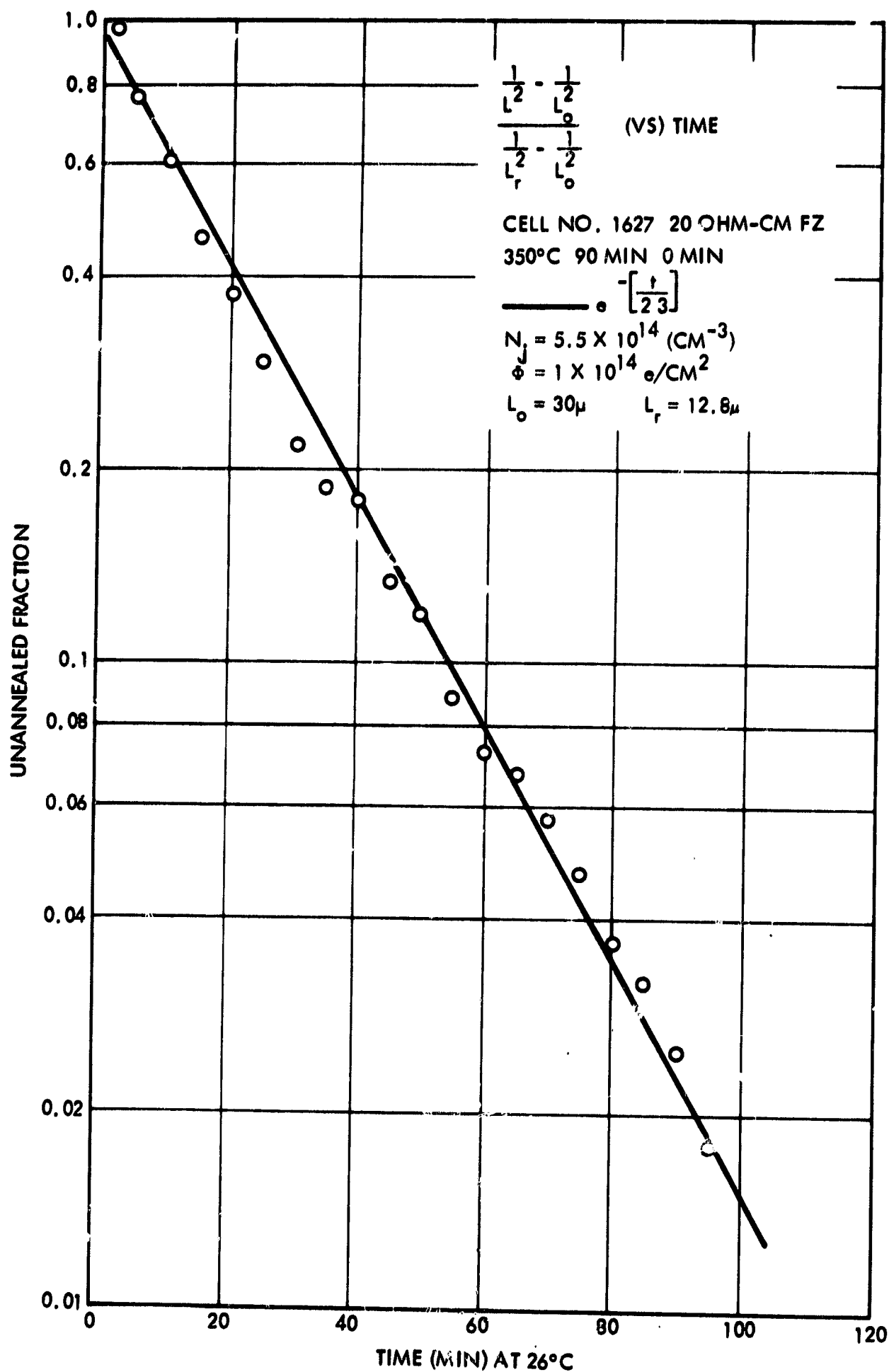


FIGURE 39. RECOVERY KINETICS OF IRRADIATED LITHIUM SOLAR CELL

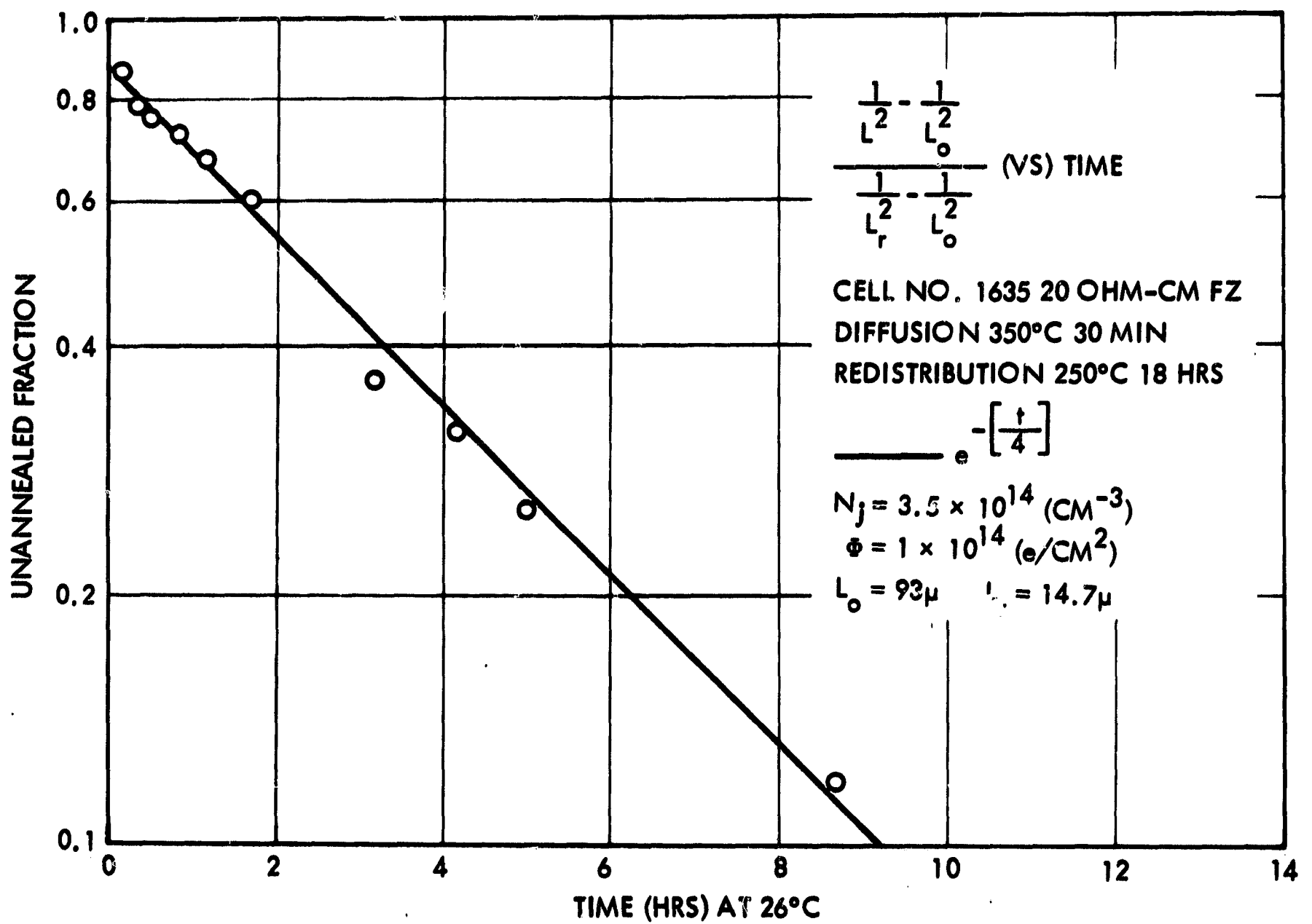


FIGURE 40. RECOVERY KINETICS OF IRRADIATED LITHIUM SOLAR CELL

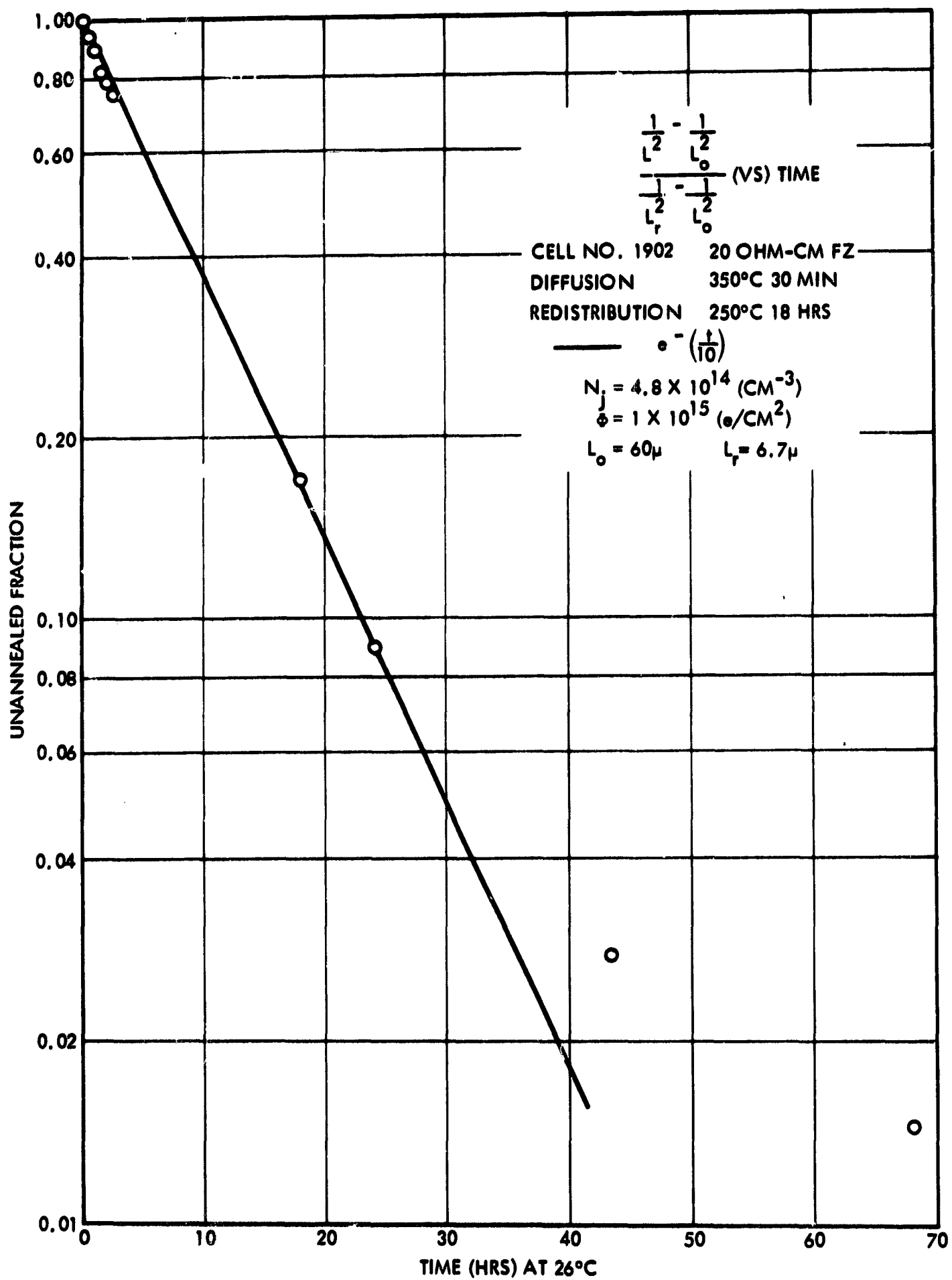


FIGURE 41. RECOVERY KINETICS OF IRRADIATED LITHIUM SOLAR CELL

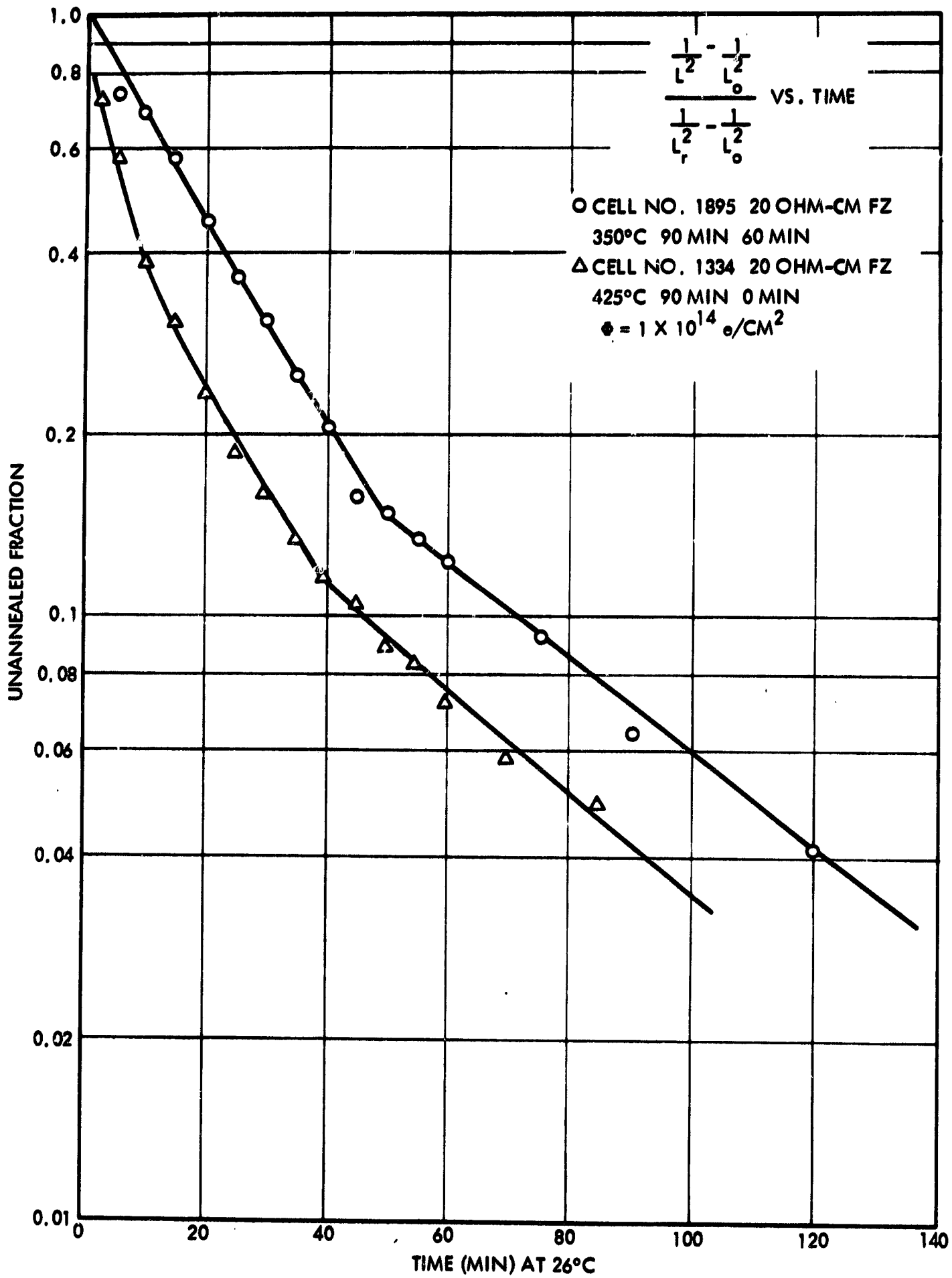


FIGURE 42. RECOVERY KINETICS OF IRRADIATED LITHIUM SOLAR CELL

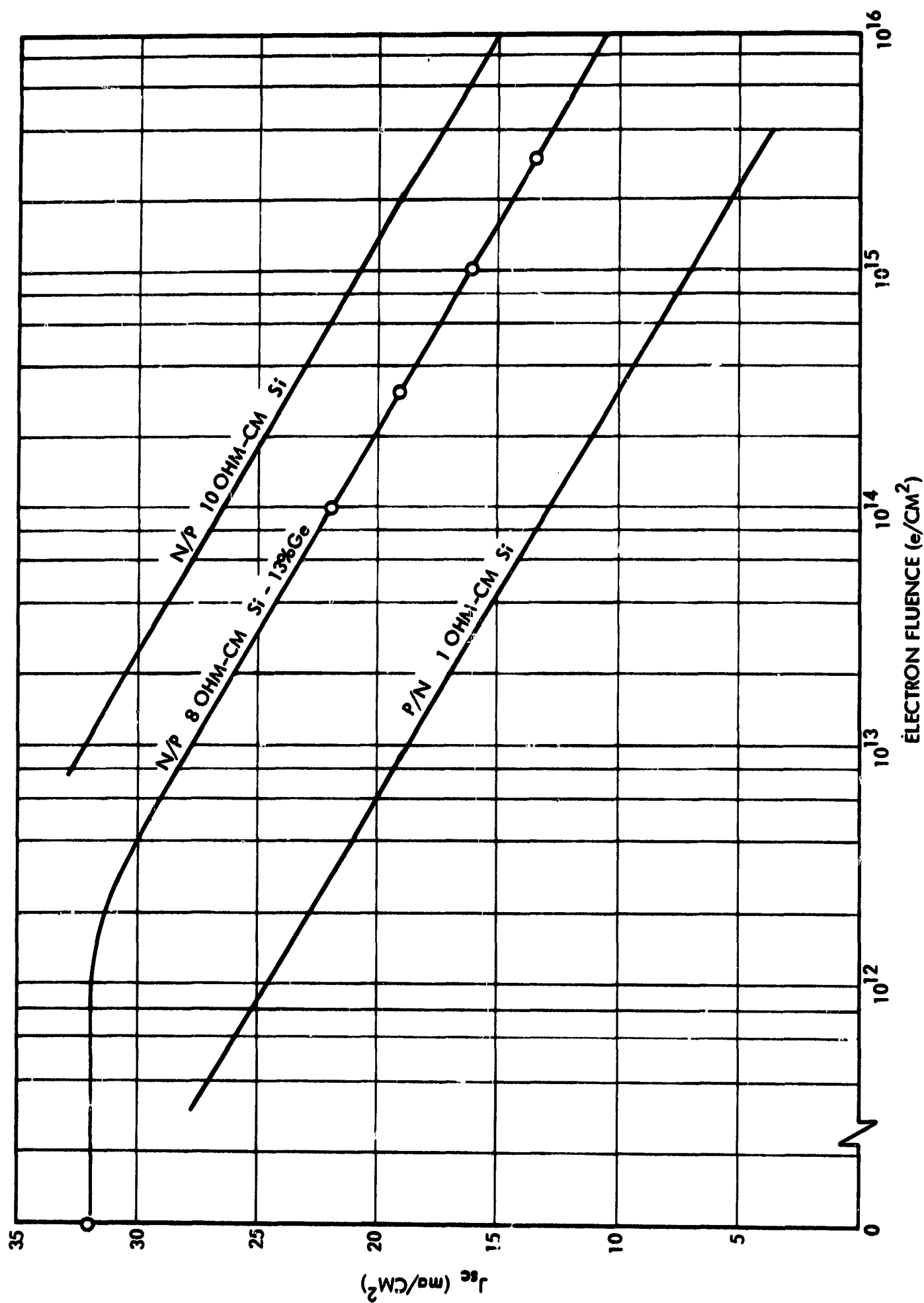


FIGURE 43. IRRADIATION OF A N/P SILICON-GERMANIUM ALLOY SOLAR CELL

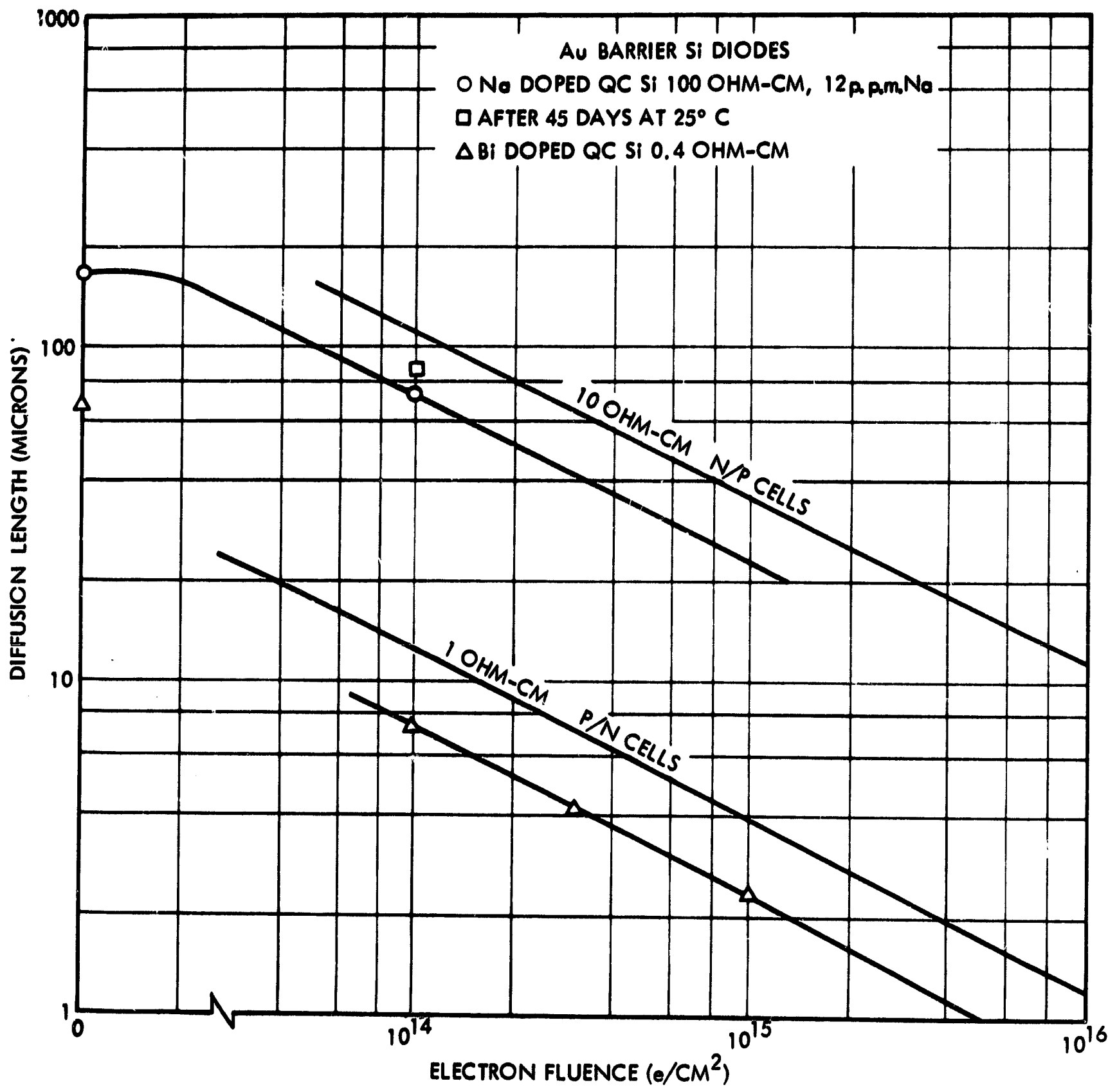


FIGURE 44. IRRADIATION OF SODIUM DOPED SILICON
AND BISMUTH DOPED SILICON